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A NOTE ON UNIQUENESS SETS FOR ENTIRE FUNCTIONS

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(Communicated by Dr. M. Ishaq, F.A.SC.)

1. A sequence $\{a_n\}_{n=1}^{\infty}$ is called a uniqueness set for entire functions of a given class, if for $f(z)$ of the class, $f(a_n) = 0$, $(n = 1, 2, \ldots.)$ implies $f(z) \equiv 0$. Let $n(r)$ denote the number of a_n with $|a_n| \leqslant r$, and let

$$\limsup_{r\to\infty} n(r)/r^{\rho} = \mathrm{L}; \quad \liminf_{k\to\infty} n(r)/r^{\rho} = l. \tag{1.1}$$

R. P. Boas, Jr. has proved two general theorems [1, pp. 22–23] which reduce the problem of fundamental sets of the forms $\mathrm{F}(a_n z)$ and $\mathrm{F}(z + a_n)$ to the problem of uniqueness sets for entire functions, and has also proved the following criteria [1, pp. 23–24] for uniqueness sets.

THEOREM A.—*The set $\{a_n\}$ is a uniqueness set for functions of order atmost ρ, type less than τ if of order ρ, if*

$$\tau \leqslant \limsup_{r\to\infty} r^{-\rho} \int_0^r t^{-1} n(t)\, dt$$

in particular if

$$\tau \leqslant l/\rho \tag{1.2}$$

or if

$$\tau \leqslant \mathrm{L}/e\rho. \tag{1.3}$$

THEOREM B.—*The set $\{a_n\}$ is a uniqueness set for functions of order atmost ρ and of type less than τ if of order ρ, if the a_n are contained in an angle of opening 2α, and either*

$$\limsup_{r\to\infty} r^{1-\frac{\alpha\rho}{b}} \int_0^{r^{\alpha/b}} n(t)\left(t^{-1-\frac{b}{\alpha}} + t^{-1+\frac{b}{\alpha}} r^{-2}\right) dt \geqslant \frac{2\alpha\tau}{\pi \mathrm{B}} \frac{\alpha^2\rho^2}{\alpha^2\rho^2 - b^2}\ ; \quad (\alpha > b/\rho)$$

or

$$\limsup_{r\to\infty} \frac{1}{\log r} \int_0^{r^{1/b}} n(t)\,(t^{-1-\rho} + t^{-1+\rho} r^{-2}\, dt) \geqslant \{\tau \sec \alpha\rho\}/\rho\pi; \quad (\alpha \leqslant b/\rho)$$

in particular if

$$\tau \leqslant (\pi B l)/\alpha\rho \qquad (\alpha > b/\rho) \tag{1·5}$$

or

$$\tau \leqslant \pi l \cos(\alpha\rho) \qquad (\alpha \leqslant b/\rho) \tag{1·6}$$

here $B = b \cos b$ *is the maximum of* $x \cos x$ *in* $(0, \pi/2)$.

In this note I give criteria for uniqueness sets more general than (1·2), (1·3) and (1·5). Let

$$\limsup_{r\to\infty} \log M(r)/r^\rho = T; \quad \liminf_{r\to\infty} \log M(r)/r^\rho = t.$$

THEOREM 1.—*The set* $\{a_n\}$ *is a uniqueness set for functions of order atmost* $\rho\,(0 < \rho < \infty)$, *and lower type* $\leqslant t$ *and type* $\leqslant T$ *if of order* ρ, *if either*

$$t < l/\rho \tag{1.7}$$

or

$$T < (e\rho)^{-1}\, L \exp(l/L) \tag{1·8}$$

in particular if

$$T < (2e\rho)^{-1}[L + l + \sqrt{(L^2 + 3l^2 + 2lL}] \tag{1·9}$$

or if

$$T < (e\rho)^{-1}(L + l) \tag{1·10}$$

or if

$$T \leqslant l/\rho; \text{ and } l < L. \tag{1·11}$$

THEOREM 2.—*The set* $\{a_n\}$ *is a uniqueness set for functions of order atmost* ρ, *and of type less than or equal to* T *if of order* ρ, *if the* a_n *are contained in an angle of opening* 2α, $b/\rho < \alpha < \pi$, *and if*

$$T < \frac{\pi BL}{\alpha\rho}\left\{1 + \frac{b(L-l)}{\rho\alpha L}\right\}^{-\frac{1}{2}\left(\frac{\alpha\rho}{b}-1\right)}\left\{1 - \frac{b(L-l)}{\rho\alpha L}\right\}^{\frac{1}{2}\left(\frac{\alpha\rho}{b}+1\right)} \tag{1.12}$$

Here B and b have the same meanings as in Theorem B.

We note that condition (1·7) implies $l > 0$ and any one of the conditions (1.8) to (1·12) implies that $L > 0$. In §5 and §6 we construct functions to show that (1.7) and (1.8) are best possible conditions.

2. Theorem 1 is equivalent to the following lemma.

LEMMA 2.1.—*If* $f(z)$ *is an entire function of order* ρ *and type* T *and lower type* t, *and if* $n(r)$ *denotes the number of zeros of* $f(z)$ *in* $|z| \leqslant r$ *and* L *and* l *have the same meanings as in* (1.1) *then*

$$l \leqslant \rho t \tag{2.2}$$

$$le \leqslant L \exp(l/L) \leqslant \rho T e \tag{2.3}$$

$$L + l + \sqrt{(L^2 + 3l^2 + 2lL)} \leqslant 2\rho T e \tag{2.4}$$

$$L + l \leqslant \rho T e \tag{2.5}$$

$$l < \rho T \text{ if } l < L \tag{2.6}$$

Proof.—By Jensen's Theorem, if $a \geqslant 1$

$$\int_0^{ra^{1/\rho}} \frac{n(x)}{x}\,dx < k + \log M(ra^{1/\rho})$$

Hence[1]

$$(l-\epsilon)\frac{r^\rho}{\rho} + n(r)\int_r^{ra^{1/\rho}} \frac{dx}{x} < k + \log M(ra^{1/\rho}) \qquad (2\cdot7)$$

and so [2, p. 82]

$$(l + L\log a)/(\rho a) \leqslant T.$$

The left-hand side is maximum when $a = \exp[(L-l)/L]$. Hence

$$T \geqslant \frac{L}{\rho e}\, e^{l/L} \geqslant \frac{L}{\rho e}\left\{1 + \frac{l}{L} + \frac{l^2}{2L^2}\right\}$$

Hence

$$T \geqslant L/(\rho e) \text{ and } \rho\, eT \geqslant L + l + l^2/(2\rho\, eT)$$

which gives

$$2\rho eT \geqslant L + l + \sqrt{(L^2 + 3l^2 + 2lL)} \geqslant 2(L + l).$$

Further taking $a = 1$ in (2.7) we get

$$l \leqslant \rho t.$$

Now e^x/x has only one minimum point, $x = 1$. Hence $e^x \geqslant ex$ equality if $x = 1$. Hence

$$e^{l/L} \geqslant (el)/L \text{ equality if } l = L$$

and so

$$T \geqslant \frac{L}{\rho e}\, e^{l/L} \geqslant \frac{l}{\rho}$$

and $T > l/\rho$ if $l < L$.

3. Theorem 2 is equivalent to the following lemma.

LEMMA 3·1.—*If $f(z)$ is of order ρ and type T, if $f(z)$ has zeros $a_n = r_n e^{i\theta_n}$ with $|\theta_n| \leqslant \alpha < \pi$, and if $n(r)$ denotes the number of a_n with $|a_n| \leqslant r$, then*[2]

$$T \geqslant \frac{\pi BL}{\alpha\rho}\left\{1 + \frac{b(L-l)}{\rho\alpha L}\right\}^{-\frac{1}{2}\left(\frac{\alpha\rho}{b}-1\right)}\left\{1 - \frac{b(L-l)}{\rho\alpha L}\right\}^{\frac{1}{2}\left(\frac{\alpha\rho}{b}+1\right)} \qquad (3.2)$$

$$\geqslant \frac{\pi Bl}{\alpha\rho}$$

$$T > (\pi Bl)/(\alpha\rho) \text{ if } l < L. \qquad (3.3)$$

Here $\alpha > b/\rho$ and L, l, B and b have the same meanings as before.

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1. k denotes a constant not necessarily the same at each occurrence.

2. We suppose in this lemma that $L > 0$. If $L = 0$ we have from (3·4) an obvious result $T \geqslant 0$.

Proof.—Let the integral in (1.4) be denoted by $I = I(r)$. Boas has proved [1, pp. 28–29] that if $\alpha > b/\rho$

$$\limsup_{R\to\infty} R^{1-\frac{a\rho}{b}} I(R) \leqslant \frac{2\alpha T}{\pi B}\frac{a^2\rho^2}{a^2\rho^2-b^2}$$

Let $0 < c < 1$. Then

$$I(R) > (l-\epsilon)\int_{r_0}^{cR^{a/b}} \{t^{\rho-1-\frac{b}{a}} + t^{\rho-1+\frac{b}{a}} R^{-2}\}\, dt$$

$$+ n(cR^{a/b})\int_{cR^{a/b}}^{R^{a/b}} (t^{-1-\frac{b}{a}} + t^{-1+\frac{b}{a}} R^{-2})\, dt.$$

Hence

$$\frac{2\alpha T}{\pi B}\frac{a^2\rho^2}{a^2\rho^2-b^2} \geqslant \limsup_{R\to\infty} R^{1-\frac{a\rho}{b}} I(R)$$

$$\geqslant l\left\{\frac{c^{\rho-\frac{b}{a}}}{\rho-\frac{b}{a}} + \frac{c^{\rho+\frac{b}{a}}}{\rho+\frac{b}{a}}\right\} + \frac{La}{b}(c^{-b/a} - c^{b/a})\, c^{\rho}. \tag{3.4}$$

The right-hand side is maximum when

$$c = \left\{\frac{L\rho a - b(L-l)}{L\rho a + b(L-l)}\right\}^{a/2b}$$

Hence we have

$$T \geqslant \frac{\pi B(a^2\rho^2-b^2)}{2a^2\rho^2}\left\{\frac{L\rho a - b(L-l)}{L\rho a + b(L-l)}\right\}^{\frac{\rho a}{2b}} \frac{\sqrt{(L^2\rho^2a^2 - b^2(L-l)^2)}}{b} \times$$

$$\left\{\frac{1}{\rho a - b} - \frac{1}{\rho a + b}\right\}$$

which proves the left-hand side of (3·2). Let the middle expression in (3.2) be denoted by M. Then

$$M \leqslant (\pi BL)/(a\rho)$$

Consider now

$$y = (1-x)^{1+\theta}(1+x)^{-\theta} - \{1-(1+2\theta)x\} \text{ where } \theta > 0,\ 0 \leqslant x \leqslant 1$$

$$\frac{dy}{dx} = (1+\theta)\left\{1 - \left(\frac{1-x}{1+x}\right)^{\theta}\right\} + \theta\left\{1 - \left(\frac{1-x}{1+x}\right)^{\theta+1}\right\} \geqslant 0$$

for all $x \leqslant 1$, equality if $x = 0$. Further $y(0) = 0$. Hence $y(x) \geqslant 0$ if $0 \leqslant x \leqslant 1$, equality if $x = 0$. Writing

$$x = \frac{b(L-l)}{\rho aL} \leqslant \frac{b}{\rho a} < 1;\ \theta = \tfrac{1}{2}\left(\frac{a\rho}{b} - 1\right) > 0$$

we obtain

$$M \geqslant \frac{\pi BL}{a\rho}\,\frac{l}{L} = \frac{\pi Bl}{a\rho}$$

equality if $L = l$ only. Hence the lemma is proved.

4. The condition (1.12) requires $\rho > b/a$ and gives a better result than (1·8) when $(L - l)/L$ is a small number and $b/\rho < a < \pi B$. If $\rho \leqslant b/a$ the corresponding condition is (1·6) which is weaker than (1.8) if $\rho \cos a\rho \leqslant 1/\pi$. This range of values of ρ, for which (1.8) will be stronger than (1·6), increases as l/L diminishes. For instance, if $l/L = 1/100$ then so long as $\rho \cos a\rho \leqslant 37/\pi$ the condition (1.8) will give a larger upper bound for T than (1.6).

5. To show that (2.2) is best possible, we construct an entire function $f(z)$ for which $l = \rho t$. For the function given by Boas [1, pp. 31–32]. $\rho t - l$ is not zero but can be made arbitrarily small.

THEOREM 3.—*For each positive ρ and each positive t, there exists an entire function $f(z)$ of order ρ, type t, with zeros a_n such that*

$$l = \liminf_{n \to \infty} n\,|a_n|^{-\rho} = \rho t. \tag{5·1}$$

Let

$$a_n = n^{2/\rho}/(2\rho t)^{1/\rho}$$

$$f(z) = \prod_{r=1}^{\infty} \left(1 + \frac{z^r}{a_r{}^r}\right) \tag{5·2}$$

We have then

$$n(a_n) = 1 + 2 + \ldots + n = \frac{n^2}{2} + O(n) \sim \rho t a_n{}^{\rho}$$

If $a_n \leqslant r < a_{n+1}$

$$n(r) = n(a_n) \sim \rho t a_n{}^{\rho} \sim \rho t r^{\rho}. \quad \text{Hence } l = \rho t.$$

Now let $r = a_n$

$$\log f(r) = \sum_{r=1}^{n-1} \log\left(1 + \frac{r^r}{a_r{}^r}\right) + \log 2 + \sum_{n+1}^{\infty} \log\left(1 + \frac{r^r}{a_r{}^r}\right)$$

$$= \Sigma_1 \qquad + \log 2 + \Sigma_2 \text{ (say)}.$$

Now

$$\Sigma_2 = \sum_{k=1}^{\infty} \log\left\{1 + \left(\frac{n}{n+k}\right)^{2(n+k)/\rho}\right\}$$

$$= \sum_{k=1}^{n} + \sum_{n+1}^{\infty} = O(n)$$

and

$$\Sigma_1 = \log \frac{a_1 + a_n}{a_1}\,\frac{a_2{}^2 + a_n{}^2}{a_2{}^2} \ldots \frac{a_{n-1}{}^{n-1} + a_n{}^{n-1}}{a_{n-1}{}^{n-1}}$$

Since

$$\nu \log (a_n/a_\nu) < \log \frac{a_n{}^\nu + a_\nu{}^\nu}{a_\nu{}^\nu} < \log 2 + \nu \log \frac{a_n}{a_\nu}$$

Hence

$$\Sigma_1 = \mathbf{O}(n) + \log \frac{a_n{}^{1+2+\ldots+(n-1)}}{a_1{}^1 a_2{}^2 \ldots a_{n-1}{}^{(n-1)}}$$

$$= \frac{n^2}{2} \log a_n + \mathbf{O}(n \log n) - \left[\sum_1^{n-1} \left(\frac{2}{\rho} k \log k - \frac{k}{\rho} \log (2\rho t) \right) \right]$$

$$= \frac{n^2}{2\rho} + o(n^2)$$

changing n to $(n+1)$

$$\log f(a_{n+1}) = \frac{n^2}{2\rho} + o(n^2)$$

Hence if $a_n \leqslant r < a_{n+1}$ we have

$$\log f(a_n) \leqslant \log f(r) < \log f(a_{n+1})$$

and so

$$\log \mathbf{M}(r) = \frac{n^2}{2\rho} + o(n^2) \sim tr^\rho.$$

6. When $l = 0$ we have from (2·3) that $\mathbf{L} \leqslant \rho \mathbf{T} e$. In this section we construct a function $f(z)$ to show that this relation is best possible. A similar function, for the same purpose, has been constructed by Boas [1, pp. 30–31]. We consider also, a particular sequence $\mathbf{R}(n) = \mathbf{R}$ such that $\log \mathbf{M}(\mathbf{R}, f) \sim \mathbf{T}\mathbf{R}^\rho$, and prove that $n(\mathbf{S}) \sim \mathbf{L}\mathbf{S}^\rho$ where $\mathbf{S} = \mathbf{S}(n) = \mathbf{R}(n) e^{-1/\rho}$ and $\mathbf{L} = \rho e \mathbf{T}$.

THEOREM 4.—*For each positive* ρ, *and each positive* T, *there exists an entire function* $f(z)$ *of order* ρ *and type* T, *with zeros* a_n *such that*

$$\mathbf{T} = \limsup_{r \to \infty} \log \mathbf{M}(r)/r^\rho = \lim_{n \to \infty} \log \mathbf{M}\{\mathbf{R}(n)\}/\{\mathbf{R}(n)\}^\rho \qquad (6\cdot1)$$

$$\mathbf{L} = \limsup_{r \to \infty} n(r)/r^\rho = \lim_{n \to \infty} n\{\mathbf{S}(n)\}/\{\mathbf{S}(n)\}^\rho = \rho e \mathbf{T} \qquad (6\cdot2)$$

$$t = \liminf_{r \to \infty} \log \mathbf{M}(r)/r^\rho = \lim_{n \to \infty} \log \mathbf{M}\{\mathbf{S}(n)\}/\{\mathbf{S}(n)\}^\rho = 0 \qquad (6\cdot3)$$

where $\{\mathbf{R}(n)\} \uparrow \infty$ and $\mathbf{S}(n) = \mathbf{R}(n) e^{-1/\rho}$

Let $\mathbf{F}(n) = 2^{\mathbf{F}(n-1)}$; $\mathbf{F}(1) = 2$ $\qquad (n = 2, 3, \ldots.)$

$\mathbf{S}(n) = \{\mathbf{F}(n)/\rho e \mathbf{T}\}^{1/\rho}$; $\mathbf{R}(n) = \mathbf{S}(n) e^{1/\rho}$; $\qquad (n = 1, 2, 3, \ldots.)$

$$f(z) = \prod_1^\infty \left\{ 1 + \left(\frac{z}{\mathbf{S}(n)} \right)^{\mathbf{F}(n)} \right\}$$

$f(z)$ is an entire function.

$$f(\mathbf{R}(n)) = \mathbf{M}(\mathbf{R}(n)) = \Pi_1 \Pi_2 \Pi_3$$

where

$$\Pi_1 = \prod_{\nu=1}^{n-1} \left\{1 + \left(\frac{\mathrm{R}(n)}{\mathrm{S}(\nu)}\right)^{\mathrm{F}(\nu)}\right\}$$

Hence

$$\frac{\log \Pi_1}{\{\mathrm{R}(n)\}^\rho} \leqslant \left\{ \{\log 2 \left(\mathrm{R}(n)\right)^{\mathrm{F}(n-1)} - \mathrm{F}(n-1) \log \left(\mathrm{S}(n-1)\right) + (n-2)\,\mathrm{F}(n-2) \log \{2\,\mathrm{R}(n)\} \right\} \{\mathrm{R}(n)\}^\rho \to 0 \text{ as } n \to \infty$$

$$\Pi_2 = \left\{1 + \left(\frac{\mathrm{R}(n)}{\mathrm{S}(n)}\right)^{\mathrm{F}(n)}\right\} = 1 + e^{\mathrm{F}(n)/\rho}$$

$$\frac{\log \Pi_2}{\{\mathrm{R}(n)\}^\rho} \sim \frac{\mathrm{F}(n)}{\rho} \frac{\rho \mathrm{T}}{\mathrm{F}(n)} = \mathrm{T}$$

Further

$$\Pi_3 = \prod_{\nu=n+1}^{\infty} \left\{1 + \left(\frac{\mathrm{R}(n)}{\mathrm{S}(\nu)}\right)^{\mathrm{F}(\nu)}\right\}$$

and

$$\left\{\frac{\mathrm{R}(n)}{\mathrm{S}(n+k)}\right\}^{\mathrm{F}(n+k)} < \left(\tfrac{1}{2}\right)^{\mathrm{F}(n+k)} \text{ if } k \geqslant 1;\ n \geqslant n_0$$

Hence

$$\Pi_3 < e^{\sum_{1}^{\infty} \left(\frac{1}{2}\right)^{\mathrm{F}(n+k)}} < e$$

and therefore

$$\lim_{n \to \infty} \frac{\log \mathrm{M}\{\mathrm{R}(n)\}}{\{\mathrm{R}(n)\}^\rho} = \mathrm{T}$$

Let now $\mathrm{S}(n) \leqslant r < \mathrm{S}(n+1)$. Then

$$f(r) = \prod_{1}^{n-1} \cdot \left[1 + \left(\frac{r}{\mathrm{S}(n)}\right)^{\mathrm{F}(n)}\right]\left[1 + \left(\frac{r}{\mathrm{S}(n+1)}\right)^{\mathrm{F}(n+1)}\right] \times \prod_{n+2}^{\infty} = \Pi_1 \Pi_2 \Pi_3 \Pi_4 \text{ (say)}$$

Then

$$\log \Pi_1 = \mathrm{o}\,(r^\rho).$$

If $r = \mathrm{S}(n)$, $\Pi_2 = 1$. If $r > \mathrm{S}(n)$ then for all large n

$$\frac{\log \Pi_2}{r^\rho} \sim \frac{\mathrm{F}(n) \log r/\mathrm{S}(n)}{r^\rho} = \frac{\mathrm{F}(n)}{\{\mathrm{S}(n)\}^\rho} \frac{\log \{r/\mathrm{S}(n)\}}{\{r/\mathrm{S}(n)\}^\rho} \leqslant \frac{\rho e \mathrm{T}}{\rho e} = \mathrm{T}$$

since $\dfrac{\log x}{x^\rho} \leqslant \dfrac{1}{\rho e}$ for all $x \geqslant 1$.

Further $\Pi_3 \leqslant 2$; $\Pi_4 < e$

Hence

$$\limsup_{r\to\infty} \frac{\log M(r)}{r^\rho} = T.$$

If $r = S(n)$, we have

$$t = \liminf_{r\to\infty} \frac{\log M(r)}{r^\rho} = \lim_{n\to\infty} \frac{\log M\{S(n)\}}{\{S(n)\}^\rho} = 0$$

Further

$$n\{S(n)\} = F(1) + \ldots + F(n) \sim F(n)$$

$$\frac{n\{S(n)\}}{\{S(n)\}^\rho} \sim \rho e T.$$

Since $L \leqslant \rho e T$ we have

$$L = \limsup_{r\to\infty} \frac{n(r)}{r^\rho} = \lim_{n\to\infty} \frac{n\{S(n)\}}{\{S(n)\}^\rho} = \rho e T.$$

Also

$$l = \liminf_{r\to\infty} \frac{n(r)}{r^\rho} = \lim_{n\to\infty} \frac{n(S(n)-1)}{\{S(n)-1\}^\rho} = 0$$

If $n > n_0$, $n\{R(n)\} = n\{S(n)\}$

and hence $\lim_{n\to\infty} n\{R(n)\}/\{R(n)\}^\rho = \rho T$.

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ON THE HARMONIC SUMMABILITY OF FOURIER SERIES

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1. Let $f(x)$ be a function integrable in the sense of Lebesgue and periodic with period 2π. Let the Fourier Series associated with $f(x)$ be

$$\tfrac{1}{2}a_0 + \sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx). \tag{1·1}$$

A sequence $\{s_n\}$ is said to be summable by *harmonic means*, if

$$\lim_{n\to\infty} \frac{1}{\log n} \sum_{k=0}^{n} \frac{s_{n-k}}{k+1} \tag{1·2}$$

exists. This method of summability which belongs to the class of generalized regular Nörlund methods*, was introduced for the first time by M. Riesz† who proved that every series summable by harmonic means is summable (C, δ), $\delta > 0$.

The application of harmonic summation to Fourier Series has been discussed by Juringius‡, Hille and Tamarkin§ and Iyengar§§. In this paper I prove the following theorem:—

THEOREM.—*The Fourier Series of the function $f(x)$ is summable by harmonic means at a point x at which*

$$g_1(t) = \int_0^t |g(u)|\,du = 0\left(\frac{t}{\log \frac{1}{t}}\right), \tag{1·3}$$

where

$$g(t) = f(x+t) + f(x-t) - 2f(x).$$

I am indebted to Dr. B. N. Prasad for his kind help and advice in the preparation of this paper.

* Nörlund (8).

† Riesz (9).

‡ A proof of the theorem that the Fourier Series is not summable by harmonic means almost everywhere had been worked out by him but remains unpublished. See Hille and Tamarkin (4), (5).

§ Hille and Tamarkin (4), (5).

§§ Iyengar (6), (7).

2. In order to prove the theorem we shall require the following lemmas:

LEMMA I*. *If* $0 < t < \pi$, *then*

$$\left|\sum_{k=0}^{n} \frac{\cos(k+1)t}{k+1}\right| < A\left(1 + \log \frac{1}{t}\right).$$

LEMMA II†. *For all values of* n *and* x

$$\left|\sum_{k=0}^{n} \frac{\sin(k+1)t}{k+1}\right| \leqslant \tfrac{1}{2}\pi + 1.$$

3. *Proof of the Theorem.* Let $s_n(x)$ denote the n-th partial sum of the series (1·1). It is well-known that

$$s_n(x) - f(x) = \frac{1}{2\pi}\int_0^{\pi} g(t)\,\frac{\sin(n+\frac{1}{2})t}{\sin\frac{1}{2}t}\,dt. \tag{3·1}$$

Making use of the formula (1·2), we obtain

$$\begin{aligned}
&\frac{1}{\log n}\sum_{k=0}^{n}\frac{1}{k+1}\{s_{n-k} - f(x)\} \\
&= \frac{1}{\log n}\sum_{k=0}^{n}\frac{1}{k+1}\cdot\frac{1}{2\pi}\int_0^{\pi} g(t)\cdot\frac{\sin(n-k+\frac{1}{2})t}{\sin\frac{1}{2}t}\,dt \\
&= \int_0^{\pi} g(t)\cdot\frac{1}{2\pi\log n}\sum_{k=0}^{n}\frac{1}{k+1}\,\frac{\sin(n-k+\frac{1}{2})t}{\sin\frac{1}{2}t}\,dt \\
&= \int_0^{\pi} g(t)\,\mathrm{N}_n(t)\,dt.
\end{aligned}$$

In order to prove the theorem we have to show that

$$\int_0^{\pi} g(t)\,\mathrm{N}_n(t)\,dt = 0(1), \tag{3·2}$$

as $n \to \infty$, when (1·3) holds.

We set

$$\begin{aligned}
\int_0^{\pi} g(t)\,\mathrm{N}_n(t)\,dt &= \Big(\int_0^{\frac{1}{n}} + \int_{\frac{1}{n}}^{\delta} + \int_{\delta}^{\pi}\Big) g(t)\,\mathrm{N}_n(t)\,dt \\
&= \mathrm{L}_1 + \mathrm{L}_2 + \mathrm{L}_3.
\end{aligned}$$

Now

$$\begin{aligned}
\mathrm{L}_1 &= \int_0^{\frac{1}{n}} g(t)\,\mathrm{N}_n(t)\,dt \\
&= \mathrm{O}\Big(\int_0^{\frac{1}{n}} |g(t)|\cdot n\,dt\Big)
\end{aligned}$$

---

* For proof refer to Hardy and Rogosinski (3).

† Gronwall (1), Titchmarsh (10), p. 440.

$$= \mathrm{O}\left(g_1\left(\frac{1}{n}\right) \cdot n\right)$$

$$= 0\left(\frac{1}{\log n}\right) = 0\,(1), \qquad (3\cdot3)$$

since $\mathrm{N}_n(t) = \mathrm{O}(n)$‡ for all t such that $0 \leqslant t \leqslant \pi$.

Also by virtue of Riemann-Lebesgue theorem and the regularity of the method of summation, we have

$$\mathrm{L}_3 = \int_{\delta}^{\pi} g(t)\, \mathrm{N}_n(t)\, dt$$

$$= 0\,(1). \qquad (3\cdot4)$$

Lastly, in order to show that $\mathrm{L}_2 = 0\,(1)$ we require a suitable estimate for the kernel $\mathrm{N}_n(t)$ in the interval $\left(\frac{1}{n}, \delta\right)$. Since

$$\mathrm{N}_n(t) = \frac{1}{2\pi \log \frac{1}{t} \cdot \sin \frac{1}{2} t} \times$$

$$\left\{\sin\left(n + \frac{3}{2}\right) t \sum_{k=0}^{n} \frac{\cos(k+1)\, t}{k+1} - \cos\left(n + \frac{3}{2}\right) t \sum_{k=0}^{n} \frac{\sin(k+1)\, t}{k+1}\right\},$$

by making use of Lemmas I and II, we get

$$\mathrm{N}_n(t) = \mathrm{O}\left[\frac{1}{t \log n}\left\{1 + \log \frac{1}{t}\right\}\right].$$

Hence

$$\mathrm{L}_2 = \int_{\frac{1}{n}}^{\delta} g(t)\, \mathrm{N}_n(t)\, dt = \mathrm{O}\left(\int_{\frac{1}{n}}^{\delta} |\, g(t)\,| \cdot |\, \mathrm{N}_n(t)\,|\, dt\right)$$

$$= \mathrm{O}\left(\frac{1}{\log n} \int_{\frac{1}{n}}^{\delta} |\, g(t)\,| \frac{dt}{t}\right)$$

$$+ \mathrm{O}\left(\frac{1}{\log n} \int_{\frac{1}{n}}^{\delta} |\, g(t)\,| \cdot \frac{1}{t} \log \frac{1}{t}\, dt\right)$$

$$= \mathrm{O}\left(\frac{1}{\log n} \cdot g_1(t) \cdot \frac{1}{t}\right]_{\frac{1}{n}}^{\delta} + \frac{1}{\log n} \int_{\frac{1}{n}}^{\delta} g_1(t) \frac{dt}{t^2}\Bigg)$$

$$+ \mathrm{O}\left(\frac{1}{\log n} \cdot g_1(t) \cdot \log \frac{1}{t} \cdot \frac{1}{t}\right]_{\frac{1}{n}}^{\delta}$$

$$+ \frac{1}{\log n} \int_{\frac{1}{n}}^{\delta} g_1(t) \cdot \left\{1 + \log \frac{1}{t}\right\} \frac{dt}{t^2}\Bigg)$$

‡ This result can be established with the help of the inequality $|\sin nt| \leqslant n\,|\sin t|$ and the relation $\sum_{k=1}^{n} \frac{1}{k+1} \simeq \log n$. See also Hille and Tamarkin (5).

$$= O\left(\frac{1}{\log n}\right) + O\left(\frac{1}{(\log n)^2}\right) + 0\left(\frac{1}{\log n}\right)$$

$$+ 0\left(\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta}\frac{dt}{t\log\frac{1}{t}}\right) + 0\left(\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta}\frac{dt}{t}\right)$$

$$= 0(1) + 0\left(\frac{\log\log\frac{1}{t}}{\log n}\Big]_{1}^{\delta}\right) + 0\left(\frac{\log\frac{1}{t}}{\log n}\Big]_{\frac{1}{n}}^{\delta}\right) = 0(1). \tag{3.5}$$

Combining (3·3), (3·4) and (3·5) we see that (3·2) holds. This proves the theorem.

4. Iyengar* has proved the undernoted theorem:—

If the series $\sum_{0}^{\infty} a_n$ *is summable by harmonic means and* $a_n > -An^{-\delta}$, $0<\delta<1$, *then the series is convergent.* It may be remarked that the theorem of this paper taken in conjunction with the above mentioned theorem of Iyengar gives another proof of the following well-known theorem of Hardy and Littlewood†:—

If (*i*) $a_n, b_n > -An^{-\delta}$ *and* (*ii*) $\int_0^t |g(u)|\,du = 0\left(\frac{t}{\log\frac{1}{t}}\right)$, *then the Fourier Series converges to* $f(x)$.

5. Iyengar‡ has proved a theorem, *viz.*,

If $g(t) = 0\left(\frac{1}{\log\frac{1}{t}}\right)$, *then the Fourier Series of* $f(x)$ *is summable by harmonic means to* $f(x)$.

This theorem of Iyengar and the theorem of this paper can both be proved indirectly by making use of a result of Hille and Tamarkin. Hille and Tamarkin§ have established the following results:—

THEOREM.—*A necessary and sufficient condition that the n-th harmonic mean of a Fourier Series shall converge to* $f(x)$ *at a point* x *at which* $\int_0^t |g(u)|\,du = 0(t)$, *is that*

$$\lim_{n\to\infty}\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta}\sin nt\cdot\log\frac{1}{t}\cdot g(t)\cdot\frac{dt}{t} = 0. \tag{5·1}$$

* Iyengar (6), Theorem I.
† Hardy and Littlewood (2).
‡ Iyengar (6), Theorem II.
§ Hille and Tamarkin (5).

If we assume Iyengar's condition, *viz.*,

$$g(t) = 0\left(\frac{1}{\log \frac{1}{t}}\right),$$

then the integral (5·1), *viz.*

$$\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} \sin nt \cdot \log \frac{1}{t} \cdot g(t)\,\frac{dt}{t} = O\left(\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} |\, g(t)\,| \cdot \log \frac{1}{t} \cdot \frac{dt}{t}\right)$$

$$= 0\left(\frac{1}{\log n}\int_{\frac{1}{n}}^{\delta} \frac{dt}{t}\right)$$

$$= 0\,(1).$$

On the other hand if we assume the condition of the theorem of this paper, *viz.*,

$$g_1(t) = \int_0^t |\, g(u)\,|\, du = 0\left(\frac{t}{\log \frac{1}{t}}\right),$$

then working on the lines of the last paragraph of § 3, it can be shown that under this condition the integral (5·1) is 0 (1). In view of the great complication and difficulty involved in establishing (5·1), the proof of the theorem as given here may be preferable.

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ON A BESSEL FUNCTION OF THE SECOND KIND AND WILKS' Z-DISTRIBUTION

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Wilks[1] studied the distribution of $Z = B\theta_1\theta_2 \ldots \theta_n$, where θ_i has the distribution

$$dF = \frac{1}{\Gamma(a_i)}\,\theta_i^{a_i-1}\,e^{-\theta_i}\,d\theta_i; \qquad (i = 1, 2, \ldots n)$$

He succeeded in integrating the distribution of Z for $n = 2$ and $a_1 = \frac{1}{2}(N-1)$ and $a_2 = \frac{1}{2}(N-2)$. Later Chung Tsi Hsu[2] derived the distribution of Z for $n = 2$ and for any values a_1 and a_2 in connection with certain tests of hypotheses for samples from two Bivariate Normal populations. The distribution is derived in the form

$$dF = \frac{2\sqrt{\pi}\,Z^{a_2-1}\,e^{-2\sqrt{(Z/B)}}\,dZ}{B^{a_2}\,\Gamma(a_1)\,\Gamma(a_2)\,\Gamma(a_1-a_2+\frac{1}{2})} \times$$

$$\int_0^\infty e^{-2x}\,2\sqrt{(Z/B)}+x^{a_1-a_2-\frac{1}{2}}\,x^{a_2-a_2-\frac{1}{2}}\,dx \qquad (1)$$

Taking $B = 1$, $a_1 = a_2 = \frac{1}{2}(N-1)$, this becomes

$$dF = \frac{2\sqrt{\pi}\,Z^{a_2-1}\,e^{-2\sqrt{Z}}\,dZ}{\Gamma^2(a_2)}\int_0^\infty e^{-2x}\,(2\sqrt{Z}+x)^{-\frac{1}{2}}\,x^{-\frac{1}{2}}\,dx \qquad (2)$$

He says " Since (2) can apparently not be simplified, I have been unable thus far to find in manageable form the distribution of the ratio $\frac{Z_1}{Z_2}$ and therefore of $\frac{u''}{u'}$. So he used the alternative criterion $\omega = Z - Z'$ (or $Z_1 - Z_2$) for the hypothesis H_1 that he considered.

2. In this paper I have derived the distribution of $\frac{Z_1}{Z_2}$ in the most general case by the use of Bessel Function of the second kind and the particular case follows immediately.

Now (1) can be written, changing the variable to $t = 2\sqrt{(Z/B)}$, and $2x = \xi$, as

$$dF = \frac{1}{2^{a_1+a_2-2}\,\Gamma(a_1)\,\Gamma(a_2)}\, t^{a_1+a_2-1} k_{a_1-a_2}(t)\,dt \tag{3}$$

where $k_\lambda(t)$ is a Bessel Function of the second kind.

Thus we have to consider a distribution of the form

$$dF = y_4\, y_0\, x^m\, k_n(x)\,dx \qquad (x > a) \tag{4}$$

The distribution given by

$$dF = y_0\, e^{-cx/b}\, |\, x\,|^m \left\{ \begin{array}{c} \pi\, I_m(x/b) \\ \text{or} \\ k_m(x/b) \end{array} \right\} dx \tag{5}$$

and

$$dF = y_0 x^m\, k_m(x)\,dx \tag{6}$$

have been studied by A. T. McKay[3] and Karl Pearson[4,5] respectively. So far I am not aware of the distribution(4) being studied.

3. *Moments of the Distribution* (4).—The constant y_0 is given by

$$1 = y_0 \int_0^\infty x^m\, k_n(x)\,dx$$

$$= y_0\, 2^{m-1}\, \Gamma\left(\frac{m+1+n}{2}\right) \Gamma\left(\frac{m+1-n}{2}\right) \ldots\ . \quad [cf.^6]$$

i.e.,

$$y_0 = 1/2^{m-1}\, \Gamma\left(\frac{m+1+n}{2}\right) \Gamma\left(\frac{m+1-n}{2}\right) \tag{7}$$

The moment generating function is

$$M(t) = y_0 \int_0^\infty e^{tx}\, x^m\, k_n(x)\,dx$$

$$= y_0 \sqrt{\frac{\pi}{2}}\, \frac{\Gamma(m-n+1)\,\Gamma(m+n+1)}{\Gamma(m+\frac{3}{2})\,(1-t^2)^{m+1}} \times$$

$$F\left(-n+\tfrac{1}{2},\ n+\tfrac{1}{2},\ m+\tfrac{3}{2},\ \tfrac{1}{2}(1+t)\right).$$

or

$$= y_0 \int_0^\infty \left\{ \sum_{r=0}^\infty \frac{t^r}{r!}\, x^{m+r}\, k_n(x) \right\} dx.$$

Integrating term by term we get

$$M(t) = y_0 \sum_{r=0}^\infty \frac{t^r}{r!} \int_0^\infty x^{m+r}\, k_n(x)\,dx$$

$$= y_0 \sum_{r=0}^\infty \frac{t^r}{r!}\, 2^{m+r-1}\, \Gamma\left(\frac{m+r+1+n}{2}\right) \Gamma\left(\frac{m+r+1-n}{2}\right) \tag{8}$$

Hence μ_r'—the rth moment about the origin is given by

$$\mu_r' = y_0\, 2^{m+r-1}\, \Gamma\left(\frac{m+r+1+n}{2}\right) \Gamma\left(\frac{m+r+1-n}{2}\right)$$

Substituting for y_0

$$\mu_r' = 2^r \frac{\Gamma\left(\frac{m+r+1+n}{2}\right) \Gamma\left(\frac{m+r+1-n}{2}\right)}{\Gamma\left(\frac{m+n+1}{2}\right) \Gamma\left(\frac{m-n+1}{2}\right)} \tag{9}$$

From (9) we get the recurrence formula

$$\mu'_{2k+1} = 2^2 \left(\frac{m+n}{2}+k\right)\left(\frac{m-n}{2}+k\right) \mu'_{2k-1} \tag{10}$$

and

$$\mu'_{2k+2} = 2^2 \left(\frac{m+n+1}{2}+k\right)\left(\frac{m-n+1}{2}+k\right) \mu'_{2k} \tag{11}$$

4. *Distribution of $v = \frac{x_1}{x_2}$ where x_1 and x_2 are distributed according to*

$$\left.\begin{aligned} f(x_1)\, dx_1 &= y_0\, x_1^{m_1}\, k_{n_1}(x_1)\, dx_1 \\ \phi(x_2)\, dx_2 &= y_0{}^1\, x_2^{m_2}\, k_{n_2}(x_2)\, dx_2 \end{aligned}\right\} \tag{12}$$

The distribution of v is given by[7] as

$$\begin{aligned} dF &= dv \int_0^\infty y_0\, y_0{}^1\, v^{m_1} x_2^{m_1} x_2\, k_{n_1}(vx_2)\, x_2^{m_2}\, k_{n_2}(x_2)\, dx_2 \\ &= y_0\, y_0{}^1\, v^{m_1}\, dv \int_0^\infty x_2^{m_1+m_2+1}\, k_{n_1}(vx_2)\, k_{n_2}(x_2)\, dx_2 \end{aligned} \tag{13}$$

It is shown that the value of the integral is[8] with proper change of symbols

$$= 2^{m_1+m_2}\, v^{n_1}\, \Gamma(\lambda)\, \Gamma(\mu) \int_0^\infty \frac{x_2^{\nu}\, dx_2}{(v^2+x_2^2)^\lambda\, (1+x_2^2)^\mu} \tag{14}$$

where

$$\lambda = \frac{m_1+m_2+n_1-n_2}{2}+1$$

$$\mu = \tfrac{1}{2}(m_1+m_2-n_1+n_2)+1$$

$$\nu = (m_1+m_2)-(n_1+n_2)+1$$

By putting $x_2 = \tan\theta$, the integral in (14) can be expanded in powers of $(1-v^2)$ and we find the value of the integral to be

$$\tfrac{1}{2} \frac{\Gamma\left(\frac{\nu+1}{2}\right) \Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{\nu+k}{2}+1\right)} \mathrm{F}\left(\frac{k+1}{2}, \lambda, \frac{\nu+k}{2}+1, a\right) \tag{15}$$

where $k = 2\mu + 2\lambda - \nu - 2$

$a = 1 - v^2$

and F is the Hypergeometric Function.

Substituting from (14) and (15) in (13), we get

$$dF = y_0 y_0^1 \, 2^{m_1+m_2-1} \frac{\Gamma(\lambda)\,\Gamma(\mu)\,\Gamma\left(\frac{\nu+1}{2}\right)\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{\nu+k}{2}+1\right)}$$

$$\times v^{m_1+m_2}\,\mathrm{F}\left(\frac{k+1}{2},\ \lambda,\ \frac{\nu+k}{2}+1,\ 1-v^2\right) dv \qquad (16)$$

where $y_0 = 1/2^{m_2-1}\,\Gamma\left(\frac{m_1+1+n_1}{2}\right)\Gamma\left(\frac{m_1+1-n_1}{2}\right)$

and $y_0^1 = 1/2^{m_2-1}\Gamma\left(\frac{m_2+1+n_2}{2}\right)\Gamma\left(\frac{m_2+1-n_2}{2}\right)$

(16) is the required distribution of x_1/x_2.

5. *Particular Cases.*—Put $m = a_1 + a_2 - 1$

$$n = a_1 - a_2$$

We have for the distribution (3) the rth moment about the origin, given by

$$\mu_r' = 2^r \frac{\Gamma\left(a_1+\frac{r}{2}\right)\Gamma\left(a_2+\frac{r}{2}\right)}{\Gamma(a_1)\,\Gamma(a_2)} \qquad (17)$$

The distribution of $v = \frac{t_1}{t_2}$ is given by, taking $m_1 = m_2 = a_1 + a_2 - 1$, $n_1 = n_2 = a_1 - a_2$ and substituting in (16)

$$dF = \frac{2\mathrm{B}(2a_1, 2a_2)}{\mathrm{B}^2(a_1, a_2)}\, v^{2a_1-1}\,\mathrm{F}(2a_1,\ a_1+a_2,\ 2a_1+2a_2,\ 1-v^2)\,dv \qquad (18)$$

where B is the Beta-Function.

In particular put $a_1 = a_2 = \frac{1}{2}(\mathrm{N}-1)$ and the constant B (in $t = 2\left(\sqrt{(\mathrm{Z}/\mathrm{B})}\right) = 1$.

Then $v = \frac{t_1}{t_2} = \sqrt{\frac{\mathrm{Z}_1}{\mathrm{Z}_2}}$ is distributed as

$$dF = \frac{2\mathrm{B}(2a_1, 2a_1)}{\mathrm{B}^2(a_1, a_1)}\, v^{2a_1-1}\,\mathrm{F}(2a_1,\ 2a_1,\ 4a_1,\ 1-v^2)\,dv \qquad (19)$$

Substituting v for v^2, we get the distribution of $\frac{\mathrm{Z}_1}{\mathrm{Z}_2}$ as

$$dF = \frac{\mathrm{B}(2a_1, 2a_1)}{\mathrm{B}^2(a_1, a_1)}\, v^{a_1-1}\,\mathrm{F}(2a_1,\ 2a_1,\ 4a_1,\ 1-v)\,dv \qquad (20)$$

which is the distribution required to test the hypothesis H_1, where Z_1 and Z_2 are dstributed according to (2).

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ON AN ABSOLUTE CONSTANT IN THE THEORY OF TAUBERIAN SERIES

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1. R. P. Agnew [1] has obtained a theorem on the Abel transform of a Tauberian series of complex terms, substantially improving a result due to H. Hadwiger [2]. By a slight generalisation of Agnew's method, we can prove an exactly similar theorem for the D (λ_n)-transform of the series of complex terms Σa_n:

$$F(s) = \sum_{\nu=1}^{\infty} a_\nu e^{-\lambda_\nu s} \; (s > 0), \; 0 = \lambda_0 < \lambda, < \lambda_2 < \ldots, \; \lambda_n \to \infty, \quad (1.1)$$

assuming, in addition to the Tauberian hypothesis:

$$\frac{\lambda_n \mid a_n \mid}{\lambda_n - \lambda_{n-1}} < K \qquad (n = 1, 2, 3, \ldots), \quad (1.2)$$

the condition

$$\lambda_n - \lambda_{n-1} = O(1) \qquad (n \to \infty). \quad (1.3)$$

In the proof of the D (λ_n)-analogue of Agnew's theorem, we write

$$A(x) = \sum_{\lambda_\nu \leqslant x} a_\nu; \quad (1.4)$$

and, in its statement, we denote by L the set of limit points, as $x \to \infty$, of $A(x)$ and by L_D the set of limit points, as $s \to +0$, of $F(s)$.

THEOREM.—*Each of the following assertions* (i), (ii) *is true when* $\rho \geqslant \rho_1$, *while the first is not necessarily true when* $\rho < \rho_1$, ρ_1 *being defined by*

$$\rho_1 = \gamma + \log\log 2 + 2\int_{\log 2}^{\infty} \frac{e^{-x}}{x}\, dx \quad (1.5)$$

where γ *is Euler's constant.*

(i) *Under conditions* (1.2) *and* (1.3) *to each* $z' \in L$ *corresponds a* $z'' \in L_D$ *such that*

$$|z' - z''| \leqslant \rho \limsup_{n \to \infty} \frac{\lambda_n |a_n|}{\lambda_n - \lambda_{n-1}}. \quad (1.6)$$

(ii) *Under conditions* (1·2) *and* (1.3), *to each* $z'' \in L_D$ *corresponds a* $z' \in L_D$ *such that* (1·6) *holds.*

2. To prove this theorem we require the three lemmas given below.

LEMMA 1.

$$\lim_{s \to +0} \left[\int_s^\infty \frac{e^{-t}}{t}\, dt + \log x + \gamma \right] = 0.$$

LEMMA 2.—*If $f(x)$ is positive, steadily decreasing, and if the strictly increasing divergent sequence $\{\lambda_n\}$ is subject to condition* (1.3), *i.e., if* $\lambda_n - \lambda_{n-1} \leqslant k$, *then*

$$\sum_{\nu=1}^{n} (\lambda_\nu - \lambda_{\nu-1}) f(\lambda_\nu) - \int_{\lambda_1}^{\lambda_n} f(x)\, dx$$

converges, as $n \to \infty$, to limit satisfying the inequalities

$$-k f(\lambda_1) \leqslant \lim_{n \to \infty} \left[\sum_{\nu=2}^{n} (\lambda_\nu - \lambda_{\nu-1}) f(\lambda_\nu) - \int_{\lambda_1}^{\lambda_n} f(x)\, dx \right] \leqslant 0. \qquad (2.1)$$

These two lemmas are easily proved by methods indicated elsewhere [1, 3] Using the second lemma we can prove

LEMMA 3.—*The series*

$$\sum_{\nu=2}^{\infty} \int_{\lambda_{\nu-1}}^{\lambda_\nu} \left(\frac{e^{-xs}}{x} - \frac{e^{-\lambda_\nu s}}{\lambda_\nu} \right) dx \equiv \sum_{\nu=2}^{\infty} \phi_\nu(s) \qquad (s > 0),$$

$$\sum_{\nu=2}^{\infty} \int_{\lambda_{\nu-1}}^{\lambda_\nu} \left(\frac{1}{x} - \frac{1}{\lambda_\nu} \right) dx \equiv \sum_{\nu=2}^{\infty} \phi_\nu(0)$$

are convergent, the first to $\Delta(s)$ and the second to C such that*

$$\lim_{s \to +0} \Delta(s) = C. \qquad (2.2)$$

Proof.—The convergence of the series $\Sigma\phi_n(s)$, $\Sigma\phi_n(0)$ is a consequence of the first half of Lemma 2. The prove (2·2) we note that $(e^{-xs} - 1)/x$, $s > 0$, is monotone increasing and therefore

$$\frac{e^{-xs} - 1}{x} \leqslant \frac{e^{-\lambda_\nu s} - 1}{\lambda_\nu} \qquad (\lambda_{\nu-1} \leqslant x \leqslant \lambda_\nu)$$

---

*We can write

$$\int_{\lambda_1}^{\infty} \frac{e^{-xs}}{x}\, dx - \sum_{\nu=2}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} = \Delta(s) \qquad (s > 0)$$

since the integral and the series separately converge.

or
$$\int_{\lambda_{\nu-1}}^{\lambda_\nu} \left(\frac{e^{-xs}}{x} - \frac{e^{-\lambda_\nu s}}{\lambda_\nu}\right) dx < \int_{\lambda_{\nu-1}}^{\lambda_\nu} \left(\frac{1}{x} - \frac{1}{\lambda_\nu}\right) dx.$$

Hence
$$0 < \phi_\nu(s) \leqslant \phi_\nu(0) \qquad (s \geqslant 0)$$
and, by Weierstrass's M-test, $\Sigma\phi_n(s)$ is uniformly convergent for $s \geqslant 0$. The last mentioned fact implies that $\Delta(s)$ is continuous for $s \geqslant 0$ and leads at once to (2.2).

3. *Proof that the asssertions of the theorem hold for* $\rho \geqslant \rho_1$.

Let us write
$$\frac{\lambda_n a_n}{\lambda_n - \lambda_{n-1}} = x_n \tag{3.1}$$
so that, in virtue of (1.2),
$$\lim_{n\to\infty} \sup |x_n| < \infty.$$
Then we have, from (1.1), (1.4) and (3.1),
$$\begin{aligned} A(\lambda_n) - F(s) &= \sum_{\nu=1}^{n} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} x_\nu - \sum_{\nu=1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} x_\nu \\ &= \sum_{\nu=1}^{n} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} (1 - e^{-\lambda_\nu s}) x_\nu - \sum_{\nu=n+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} x_\nu \\ &= \sum_{\nu=1}^{\infty} a_\nu(n, s) x_\nu \end{aligned} \tag{3.2}$$
where
$$a_\nu(n, s) = \begin{cases} (\lambda_\nu - \lambda_{\nu-1})(1 - e^{-\lambda_\nu s})/\lambda_\nu & (1 \leqslant \nu \leqslant n), \\ -(\lambda_\nu - \lambda_{\nu-1}) e^{-\lambda_\nu s}/\lambda_\nu & (\nu > n). \end{cases}$$
And so
$$\begin{aligned} \sum_{\nu=1}^{\infty} |a_\nu(n, s)| &= \sum_{\nu=1}^{n} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} (1 - e^{-\lambda_\nu s}) + \sum_{\nu=n+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} \\ &= \sum_{\nu=1}^{n} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} - \sum_{\nu=1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} + 2 \sum_{\nu=n+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} \\ &= \left[1 + \int_{\lambda_1}^{\lambda_n} \frac{dx}{x} - \sum_{\nu=2}^{n} \phi_\nu(0)\right] - \left[e^{-\lambda_1 s} + \int_{\lambda_1}^{\infty} \frac{e^{-xs}}{x} dx - \Delta(s)\right] \\ &\quad + 2\left[\int_{\lambda_n}^{\infty} \frac{e^{-xs}}{x} dx - \Delta_n(s)\right] \end{aligned} \tag{3.3}$$

where the first two square-bracketed expresions are obtained by using Lemma 3 and the third expression by a similar method; also $\Delta_n(s)$ is such that $\Delta_1(s) \equiv \Delta(s)$ and, under the condition $\lambda_n - \lambda_{n-1} \leqslant k$,

$$|\Delta_n(s)| \leqslant k e^{-\lambda_n s}/\lambda_n < k/\lambda_n.^* \tag{3.4}$$

Using (3.4) in (3.3) and putting $xs = t$ in the three integrals in (3.3), we get

$$\sum_{\nu=1}^{\infty} |a_\nu(n, s)| = (1 - e^{-\lambda_1 s}) + [\Delta(s) - \sum_{\nu=2}^{n} \phi_\nu(0)] - \left[\log \lambda_1 s + \int_{\lambda_1 s}^{\infty} \frac{e^{-t}}{t}\, dt\right] \tag{3.5}$$

$$+ \left[\log \lambda_n s + 2 \int_{\lambda_n s}^{\infty} \frac{e^{-t}}{t}\, dt\right] + O\left(\frac{1}{\lambda_n}\right) \qquad (n \to \infty).$$

Suppose that $n = n(s)$ is chosen so that $\lambda_n s \leqslant \tau < \lambda_{n+1} s$ and therefore $\lambda_n s \to \tau$ as $s \to +0$; and set

$$a_\nu(n(s), s) = \beta_\nu(s),$$

$$\gamma + \log \tau + 2 \int_{\tau}^{\infty} \frac{e^{-t}}{t}\, dt = \mathrm{P}(\tau). \tag{3.6}$$

Then

$$\lim_{s \to +0} \beta_\nu(s) = 0 \qquad (\nu = 1, 2, 3, \ldots). \tag{3.7}$$

Further, as a result of (2.2) and Lemma 1, (3.5) yields, as $s \to +0$,

$$\lim_{s \to +0} \sum_{\nu=1}^{\infty} |\beta_\nu(s)| = \mathrm{P}(\tau). \tag{3.8}$$

Finally (3.2) can be written in terms of s:

$$A(\tau/s) - F(s) = \sum_{\nu=1}^{\infty} \beta_\nu(s)\, x_\nu$$

and this relation, in conjunction with (3.7) and (3.8), leads to

$$\limsup_{s \to +0} |A(\tau/s) - F(s)| \leqslant \mathrm{P}(\tau) \limsup_{n \to \infty} |x_n|. \tag{3.9}$$

The best value of τ in (3·9) is evidently that which makes $\mathrm{P}(\tau)$ minimum. This value is seen to be $\tau = \log 2$ and to correspond to $\mathrm{P}(\tau) = \rho_1$, the number defined in (1.5). Therefore from (3.9) we deduce that

$$\limsup_{s \to +0} |A(\log 2/s) - F(s)| \leqslant \rho_1 \limsup_{n \to \infty} |x_n|. \tag{3·10}$$

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* To prove (3·4) we have only to choose $f(x) = e^{-xs}/x$ in (2·1) and the lower limits of summation and integration to be $\nu = n + 1$ and λ_n respectively, instead of $\nu = 2$ and λ_1.

To prove that assertions (i) and (ii) are true when $\rho = \rho_1$, consider a limit point of $z\,A(x)$ [or of $F(s)$]. Then there is a sequence $s_1, s_2, \ldots$ such that $s_\nu \to +0$ and $A(\log 2/s_\nu) \to z$ [or $F(s_\nu) \to z$]. From this and (3.10) we deduce that $F(s_\nu)$ [or $A(\log 2/s_\nu)$] is bounded and therefore there is a subsequence $S_1, S_2, \ldots$ such that $F(S_\nu)$ [or $A(\log 2/S_\nu)$] has a limit w and when $s \to +0$ over the subsequence, (3·10) gives

$$|z - w| \leqslant \rho_1 \limsup_{n\to\infty} \frac{|a_n|\lambda_n}{\lambda_n - \lambda_{n-1}}.$$

Thus assertions (i), (ii) are true for $\rho = \rho_1$ and necessarily so for $\rho > \rho_1$ as well.

4. We can prove that, when $\rho < \rho_1$, assertion (i) is false for a *given* $\{\lambda_n\}$, by means of a Gegenbeispiel modelled on that of Agnew [1, §§ 4, 5] but modified to suit our requirements, in the light of the preceding arguments. The Gegenbeispiel itself rests on Lemma 5 below which in its turn rests principally on Lemma 1 and

LEMMA 4.—*Suppose that* $0 < \epsilon < \frac{1}{2}$, *that* $\mathrm{P}(\tau)$ *is the function defined by* (3·6) *and* $\rho_1 = \mathrm{P}(\log 2)$ *the constant defined by* (1.5). *Then*

$$-\mathrm{P}(\tau) + J(\tau) \equiv -\mathrm{P}(\tau) + \int_{\lambda\tau}^{\infty} \frac{e^{-t}}{t}\,dt < -\rho_1 + K\epsilon + \epsilon$$

when $\lambda > \lambda_0(\epsilon) > 1$, K *being a constant.*

Proof.—The extrema of $-\mathrm{P}(\tau) + J(\tau)$ correspond to the roots of the equation

$$\tau[-\mathrm{P}'(\tau) + J'(\tau)] \equiv -1 + 2e^{-\tau} - \frac{e^{-\lambda\tau}}{\lambda} = 0.$$

As $\lambda \to \infty$, $e^{-\lambda\tau}/\lambda \to 0$ uniformly and the equation has a single root which tends to value $\log 2$. Denoting this root by $\log \overline{2+h}$ we see that $|h| < \epsilon$ when $\lambda > \lambda_1(\epsilon) > 1$; and that the root corresponds to the maximum of $-\mathrm{P}(\tau) + J(\tau)$. Hence

$$-\mathrm{P}(\tau) + J(\tau) \leqslant -\mathrm{P}(\log \overline{2+h}) + \int_{\lambda \log \overline{2+h}}^{\infty} \frac{e^{-t}}{t}\,dt \qquad (|h| < \epsilon),$$

for $\lambda > \lambda_1(\epsilon)$. Further

$$\int_{\lambda \log \overline{2+h}}^{\infty} \frac{e^{-t}}{t}\,dt < \int_{\lambda \log (\frac{3}{2})}^{\infty} \frac{e^{-t}}{t}\,dt < \epsilon$$

for $\lambda > \lambda_2(\epsilon)$. And therefore, for $\lambda > \max(\lambda_1, \lambda_2)$,

$$\begin{aligned} -P(\tau) + J(\tau) &< -P(\log 2 + h) + \epsilon \\ &< -P(\log 2) + K\epsilon + \epsilon \end{aligned}$$

which is the conclusion sought.

LEMMA 5.—*Let* $0 < \epsilon_1 < \frac{1}{2}$. *Let* Σa_n *be the (real) series*

$$0 + 0 + \ldots + 0 + \xi_p + \sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} - \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} + 0 + 0 + \ldots \tag{4.1}$$

where $\{\lambda_n\}$ *satisfies* (1·3) *in the form* $\lambda_n - \lambda_{n-1} \leqslant k$,

$$\xi_p = -\sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} + \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu}, \tag{4.2}$$

and q, m *are the least integers satisfying*

$$\lambda - \frac{k/2}{\lambda_p} \leqslant \frac{\lambda_q}{\lambda_p} < \lambda + \frac{k/2}{\lambda_p}, \tag{4.3}$$

$$\lambda - \frac{k/2}{\lambda_q} \leqslant \frac{\lambda_m}{\lambda_q} < \lambda + \frac{k/2}{\lambda_q}, \tag{4.4}$$

with reference to p *and a (suitably large)* λ. *Then, we can choose* p, λ, *at the same time fixing* q, m *as in* (4.3), (4.4), *so that the series* Σa_n *in* (4.1) *satisfies the following conditions (in the notation of* §1).

$$A(\lambda_n) < \log \lambda + 2\epsilon_1 \ (n = 1, 2, \ldots), \ A(\lambda_0) > \log \lambda - 2\epsilon_1, \tag{4.5}$$

$$F(s) < 6\epsilon_1 + K_1\epsilon_1 + \log \lambda - \rho_1 \qquad (s > 0). \tag{4.6}$$

Proof.—From (4.2)

$$\xi_p = -\int_{\lambda_p}^{\lambda_0} \frac{dx}{x} + \delta_p + \int_{\lambda_q}^{\lambda_m} \frac{dx}{x} - \delta_q$$

where $|\delta_p| < k/\lambda_p$,* $|\delta_q| < k/\lambda_q$. Hence

$$\begin{aligned} |\xi_p| &\leqslant \log\left(\frac{\lambda_m}{\lambda_q}\Big/\frac{\lambda_q}{\lambda_p}\right) + |\delta_p| + |\delta_q| \\ &< \log[(\lambda + 2^{-1}\lambda_p^{-1}k)/(\lambda - 2^{-1}\lambda_p^{-1}k)] + |\delta_p| + |\delta_q| \end{aligned} \tag{4.7}$$

on account of (4.3) and (4.4).

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* In the notation of Lemma 3, $\delta_p = \sum_{\nu=p+1}^{q} \phi_\nu(0)$. That $|\delta_p| < k/\lambda_p$ follows from (2.1) before the limit operation provided we take $f(x) = 1/x$ and the lower limits of summation and integration to be $\nu = p + 1$ and λ_p respectively.

Next, the definition of $F(s)$ gives, for our series (4.1),

$$F(s) = 0 + 0 + \ldots + 0 + \xi_p e^{-\lambda_p s} + \sum_{\nu=p+1}^{q} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} - \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} + 0 + 0 \ldots$$

$$= \xi_p e^{-\lambda_p s} + \sum_{\nu=p+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} - 2 \sum_{\nu=q+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} + \sum_{\nu=m+1}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s}$$

$$= \xi_p e^{-\lambda_p s} + \int_{\lambda_p}^{\infty} \frac{e^{-xs}}{x}\, dx - \Delta_p(s) - 2\int_{\lambda_q}^{\infty} \frac{e^{-xs}}{x}\, dx + 2\,\Delta_q(s) + \int_{\lambda_m}^{\infty} \frac{e^{-xs}}{x}\, dx - \Delta_m(s) \qquad (4.8)$$

where $|\Delta_n(s)| < k/\lambda_n$ $(n = p, q, m)$ from (3.4) and

$$\int_{\lambda_q}^{\infty} \frac{e^{-xs}}{x}\, dx = \int_{\tau}^{\infty} \frac{e^{-t}}{t}\, dt \qquad (\tau = \lambda_q s), \qquad (4.9)$$

$$\int_{\lambda_p}^{\infty} \frac{e^{-xs}}{x}\, dx < \int_{\tau/(\lambda + 2^{-1}\lambda_p^{-1}k)}^{\infty} \frac{e^{-t}}{t}\, dt = I^* \quad \text{(say)}, \qquad (4.10)$$

$$\int_{\lambda_m}^{\infty} \frac{e^{-xs}}{x}\, dx < \int_{\tau(\lambda - 2^{-1}\lambda_p^{-1}k)}^{\infty} \frac{e^{-t}}{t}\, dt = J^* \quad \text{(say)}, \qquad (4.11)$$

the last two inequalities being obtained by the use of (4.3) and (4.4). We can first choose p so that

$$|\delta_p| + |\delta_q| + |\Delta_p(s)| + 2|\Delta_q(s)| + |\Delta_m(s)| < \epsilon_1 \qquad (4.12)$$

and then λ' so that, for $\lambda > \lambda'$,

$$\log(\lambda + 2^{-1}\lambda_p^{-1}k) < \log\lambda + \epsilon_1,\ \log(\lambda - 2^{-1}\lambda_p^{-1}k) > \log\lambda - \epsilon_1, \qquad (4.13)$$

$$I^* < \epsilon_1 - \log[\tau/(\lambda + 2^{-1}\lambda_p^{-1}k)] - \gamma \qquad (4.14)$$

$$< 2\epsilon_1 + \log\lambda - \log\tau - \gamma, \qquad (4.15)$$

appealing to Lemma 1 in justification of (4.14) and then deducing (4.15) form (4.14) by means of (4·13). Further, using (4.13) and (4.12) in (4.7), we see that

$$|\xi_p| < 3\epsilon_1 \qquad (\lambda > \lambda'). \qquad (4.16)$$

Also, using (4.9), (4.10), (4.11), (4.15), (4.16) in (4.8), we get

$$F(s) < 5\epsilon_1 + \log\lambda - \mathrm{P}(\tau) + J^* \qquad (\lambda > \lambda') \qquad (4.17)$$

while, arguing as in Lemma 4, we can find λ'' such that

$$-\mathrm{P}(\tau) + J^* < -\rho_1 + K_1\epsilon_1 + \epsilon_1 \qquad (\lambda > \lambda''). \qquad (4.18)$$

Hence there is a $\lambda > \max(\lambda', \lambda'')$ for which (4.17), (4.18) both hold and together give rise to (4.6).

It remains to prove (4.5). For this purpose, we have only to recall that, as a result of (4.4),

$$A(\lambda_n) \leqslant \sum_{\nu=q+1}^{m} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} \qquad (n = 1, 2, 3, \ldots.)$$

$$= \int_{\lambda_q}^{\lambda_m} \frac{dx}{x} - \delta_q < \log(\lambda + 2^{-1}\lambda_p^{-1}k) + \epsilon_1 \qquad (\lambda > \lambda'),$$

$$A(\lambda_q) = \int_{\lambda_q}^{\lambda_m} \frac{dx}{x} - \delta_q > \log(\lambda - 2^{-1}\lambda_p^{-1}k) - \epsilon_1 \qquad (\lambda > \lambda'),$$

and then appeal to (4.13). This concludes the proof of Lemma 5.

It is obvious, but relevant to the sequel, that the series Σa_n in (4.1) satisfies the conditions

$$\limsup_{n\to\infty} \frac{\lambda_n}{\lambda_n -} \frac{|a_n|}{\lambda_{n-1}} = 1, \quad \lim_{n\to\infty} A(\lambda_n) = 0.$$

5. *Proof that, when* $\rho < \rho_1$, *assertion* (i) *is false.* This may be based on the fact that it is easy to adapt the reasoning of Agnew [1, §5] to a series constructed as follows.

Denote the series Σa_n of Lemma 5 by $\Sigma a_p(n)$; and its $D(\lambda_n)$-transform by $F_p(s)$. Choose an increasing sequence of integers $p_1, p_2, \ldots.$ (with $p_1 = p$ and λ as in Lemma 5) so that associated with it there is a positive decreasing null sequence $s_1, s_2, \ldots.$ satisfying the following conditions for each $r = 1, 2, \ldots.$

$$\lambda_{p_{r+1}} > (\lambda + 2^{-1}\lambda_{p_1}^{-1}k)^2 \lambda_{p_r},$$

$$\sum_{j=1}^{r} |F_{p_j}(s)| < \epsilon_1 \qquad (0 < s \leqslant s_r),$$

$$\sum_{\nu=p_{r+1}}^{\infty} \frac{\lambda_\nu - \lambda_{\nu-1}}{\lambda_\nu} e^{-\lambda_\nu s} < \epsilon_1 \qquad (s > s_r).$$

It is readily verified that such a choice of $\{p_r\}$ and $\{s_r\}$ is possible and (by the use of Lemma 5) that the series obtained by the termwise addition of $\Sigma a_{p_1}(n), \Sigma a_{p_2}(n), \ldots.$, falsifies assertion (i) of the theorem in §1 for $\rho < \rho_1$.

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AZOIC DYES*

Part IX. The Behaviour of ω-Benzoyl-2-acetyl-1-naphthol towards Diazonium Salts

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The members of the Naphtol AS series derived from 2-hydroxy-3-naphthoic acid and similar *o*-hydroxycarboxylic acids yield orange, red and deeper colours. The attachment of an arylazo group to a carbon atom in an aliphatic group being one method for preparing yellow dyes, the I.G. in 1921 introduced Naphtol AS–G, which is bisacetoacet-*o*-tolidide, as a "naphthol" for the production of yellow shades; coupled on the fibre with diazotised chloranilines lemon-yellow shades could be obtained. The poor substantivity and the moderate light fastness of the Naphtol AS–G shades then led to the introduction of Naphtol AS–LG, L_3G and L_4G, the constitution of which has been elucidated by Desai and Mehta.[1] The first two are arylides of terephthaloyl diacetic acid and the last is 2-acetoacetamido-6-ethoxybenzthiazole. With specified diazonium salts the bright yellow shades from Naphtol AS–L_4G possess very high light fastness. It is to be noted, however, that on account of its adequacy for general purposes Naphtol AS–G continues to be widely used for dyeing yellow azoic shades.

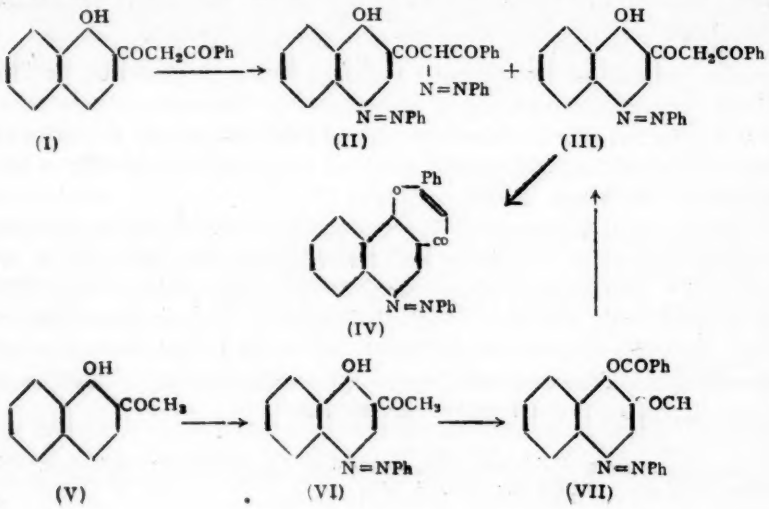
The present work is an investigation of the utility, as azoic coupling components, of diketones prepared by the action of sodamide,[2] potassium carbonate[3] or sodium ethoxide[4] on *o*-benzoyloxyaryl methyl ketones. A substance such as 2-benzoylacetyl-1-naphthol (I) has two coupling positions, and the comparative reactivity of these sites for diazonium couplings is of interest. Further, the introduction of a 1:3-diketone group in a dye or a 2-hydroxy-3-naphthanilide type of coupling component might offer a useful method for modifying shades.

2-Benzoylacetyl-1-naphthol (I) was obtained by the action of anhydrous potassium carbonate in toluene on 2-acetyl-1-naphthol benzoate in very good yield.[2] The diketone (I) gave weak dyeings when used as a "naphthol" and coupled with diazotised Fast Red Base B (5-nitro-*o*-anisidine) and Scarlet Base GG (2:5-dichloroaniline); the shades lacked fastness to soaping and light. Treatment of the dyeings with potassium dichromate and copper sulphate did not improve the fastness.

* The earlier papers of this series have appeared as "Studies in the Naphtol AS series" (for Part VIII, see *J. Sc. Ind. Res.*, 1945, 3, 447).

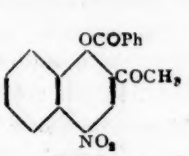
The diketone (I), when coupled in substance with one or more moles of diazotised aniline in alcoholic sodium hydroxide solution, yielded the disazo dye (II). Coupling in alcoholic sodium carbonate or pyridine solution with diazotised aniline (1 mole) yielded a mixture of the disazo dye (II) and a monoazo dye (III), which were separated by careful fractional crystallisation from acetic acid, the latter being less soluble. It was observed that boiling the monoazo dye (III) with acetic acid for a long time during crystallisation yielded a third product, which was ultimately found to be the corresponding flavone (IV). The monoazo dye (III), when dyed as a 'naphthol', and developed with diazotised Fast Red Salt B, gave brown shades which bled considerably during soaping.

The disazo dye was unaffected by treatment with concentrated sulphuric acid in the cold, while the monoazo dye, either by treatment with concentrated sulphuric acid in the cold or by refluxing with glacial acetic acid gave the flavone (IV) by cyclisation. In view of the ring closure taking place only in the case of the monoazo dye, it is evident that the coupling must have taken place in the 4-position. However, to confirm the constitution of the monoazo dye as (III), it was also prepared by an unambiguous method. 2-Acetyl-1-naphthol (V) was coupled with diazotised aniline to obtain 4-benzeneazo-2-acetyl-1-naphthol (VI). Condensation of (VI) with ethyl benzoate in presence of sodium, sodium ethoxide or sodamide was not successful. The benzoate (VII), prepared under the conditions specified, readily underwent rearrangement with potassium carbonate in toluene, and

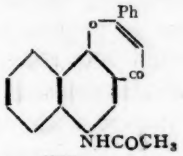


gave 4-benzeneazo-2-benzoylacetyl-1-naphthol (III) identical with the monoazodye obtained by coupling (I) with diazotised aniline. It was observed that 4-nitro-2-acetyl-1-naphthol benzoate (VIII), prepared by the benzoylation of 4-nitro-2-acetyl-1-naphthol, did not undergo rearrangement to the corresponding diketone under these conditions.

The benzeneazo-naphtha flavone (IV) on reduction with acetic acid and zinc dust, gave the acetamido derivative (IX). Even when the reduction was carried out in a large volume of alcohol with the addition of 1–2 moles of acetic acid, the acetamido derivative (IX), and not the amine (X), was obtained. Reduction with iron and hydrochloric acid in alcoholic solution gave amorphous red products. The deacetylation of (IX) proved difficult since it remained unaffected when treated either with 30 per cent. hydrochloric acid or 10 per cent. sodium hydroxide solution. The aminoflavone (X) could however be very readily obtained by reduction of (IV)



(VIII)



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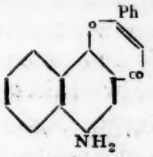


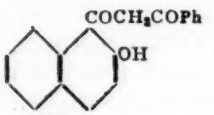
(X)

by hydrogen under pressure in presence of Raney nickel. When the diketone (III) was reduced under these conditions, the corresponding amine could not be isolated since it was very unstable. However, when (III) was reduced with sodium hydrosulphite in alcoholic alkali, the aminoflavone (X) was obtained, reduction of the azo-group and cyclisation of the diketone taking place simultaneously.

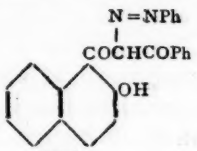
When the diketone (I) was coupled with diazotised 2:5-dichloroaniline (1 mole.) in pyridine or alcoholic sodium hydroxide solution, it gave the disazodye (II; $C_6H_3Cl_2$ instead of Ph). However, coupling in alcoholic sodium carbonate solution with diazotised 2:5-dichloroaniline (1 mole.) gave the disazo dye (II; $C_6H_3Cl_2$ instead of Ph), together with about 5 per cent. of the monoazo dye (III; $C_6H_3Cl_2$ instead of Ph), which was isolated as the flavone (IV; $C_6H_3Cl_2$ instead of Ph). The same monoazo dye was also obtained by the rearrangement of (VII; $C_6H_3Cl_2$ instead of Ph) with potassium carbonate in toluene.

In order to prepare a diketone which does not have a nuclear site for coupling as in (I), ω-benzoyl-1-acetyl-2-naphthol (XI) was prepared by the rearrangement of 1-acetyl-2-naphthyl benzoate with sodium ethoxide.[4]

The diketone (XI) when coupled in sodium hydroxide solution with diazotised aniline gave a red substance, which appeared to be a mixture of the desired azo dye (XII) and 1-benzeneazo-2-naphthol. 1-Acetyl-2-naphthol undergoes a similar displacement on treatment with diazonium salts.[5] Application of (XI) in azoic dyeing by the normal process of impregnation from an aqueous alkaline solution was not possible. The diketone (XI) coupled readily in alcohol-sodium acetate solution and gave ω-benzoyl-ω-benzeneazo-1-acetyl-2-naphthol (XII); but on account of the influence



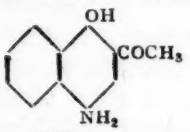
(XI)



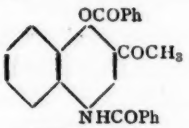
(XII)

of alcohol in lowering the substantivity of the diketone towards cellulose, a very weak yellow shade, loose to soaping, was obtained when (XI) was applied to cotton yarn from an alcoholic sodium acetate solution and developed with diazotised 2:5-dichloroaniline.

With a view to studying the effect of a benzamido group *p*- to the hydroxyl in the diketone (I), the synthesis of (XV) was then undertaken. 4-Benzamido-1-naphthol did not undergo the Nencki reaction to give the 2-acetyl compound, from which (XV) could be prepared. The azo dye from acetonaphthol and diazotised metanilic acid was reduced by alkaline sodium hydrosulphite to give the aminonaphthol (XIII), which on treatment with excess of benzoyl chloride gave the dibenzoyl derivative (XIV). Rearrangement of (XIV) with potassium carbonate in toluene gave the diketone



(XIII)



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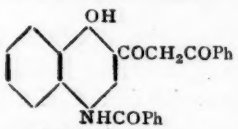
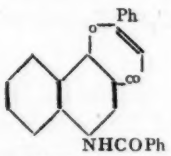
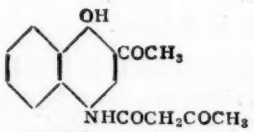


(XV)

(XV). As a "naphthol" (XV) gave a pink shade with diazotised α-aminoanthraquinone, which was loose to soaping and had a light fastness of only



(XVI)

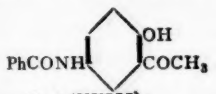


(XVII)

2-3. The diketone (XV) on treatment with concentrated sulphuric acid in the cold gave 6-benzamido-7: 8-benzoflavone (XVI).

Condensation of (XIII) with ethyl acetoacetate gave (XVII); the yellowish brown shades produced by development with diazonium salts had poor fastness to light.

5-Benzamido-2-hydroxyacetophenone (XVIII) was prepared by the Fries migration of 4-benzamidophenyl acetate. The benzoate of (XVIII) on treatment with sodamide in benzene gave the diketone (XIX). The diketone was not substantive to cotton, and when developed with diazotised dichloroaniline, it gave a weak brown shade with poor light fastness. The diketone (XIX) could be cyclized as usual to 6-benzamido-flavone (XX).



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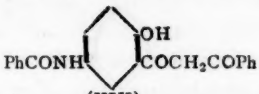

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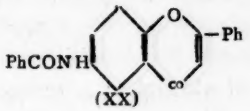

(XX)

Experimental

2-*Benzoylacetyl*-1-*naphthol* (*I*)

2-Acetyl-1-naphthyl benzoate (15 g.), toluene (75 c.c.) and freshly ignited potassium carbonate (45 g.) were refluxed under stirring for 8 hours. The deep orange potassium salt was filtered and treated with dilute acetic acid. The diketone (12 g.) crystallised from acetone in bright orange needles, m.p. 147° (Mahal and Venkataraman,[2] 147°).

Coupling of the diketone (*I*) *with diazotised aniline*

The diketone (1·5 g.) was pasted with 10% sodium hydroxide solution (10 c.c.) and dissolved in alcohol (50 c.c.). The solution was diluted with water (10–15 c.c.) and after adding sodium acetate (4 g.), cooled to 0° and coupled with aniline (1·5 g., 3 mols.) in hydrochloric acid (4·5 c.c.) diazotised with sodium nitrite (1·2 g.). The bright red dye (2·1 g.) crystallized from acetic acid in thin, elongated plates, m.p. 168–70° (Found: N, 11·2 $C_{31}H_{22}O_3N_4$ requires N, 11·2%). A little more of the disazo dye was obtained from the filtrate by acidification. The substance also crystallised from the same solvent in a second form with m.p. 204–5°. It gives a brown colour with ferric chloride and a deep cherry red colour with concentrated sulphuric acid. The dye was recovered unchanged from its solution in concentrated sulphuric acid, no cyclization to a flavone taking place under the usual conditions.

When the diketone was coupled under similar conditions using one mole of diazotised aniline, the dye that separated out proved to be (II). The

filtrate on acidification gave a sticky substance, which dissolved in concentrated sulphuric acid with a bright green fluorescence, indicating the presence of unreacted diketone.

When the diketone (I) (0·5 g.) in 10% sodium carbonate solution (10 c.c.), alcohol (100 c.c.) and sodium acetate (1 g.), was coupled with diazotised aniline (1 mol.) and stirred for one hour, a deep red solution was obtained which was acidified with dilute hydrochloric acid and the orange red dye collected (0·6 g.). The dye was taken up in acetic acid (20 c.c.), heated to about 110° and the resulting mixture was filtered immediately. The residue (0·2 g.) crystallised from alcohol-acetic acid mixture in thin short orange rods, m.p. 201–2° (Found: N, 7·3. $C_{25}H_{18}O_3N_2$ requires N, 7·2%). The monoazo dye gives a brown colour with ferric chloride and a cherry red colour with concentrated sulphuric acid. From the acetic acid mother-liquors, the disazo dye (II), m.p. 168–70°, was recovered.

The diketone (I) (0·5 g.) was then dissolved in pyridine (20 c.c.) and coupled with one mol. of diazotised aniline. The dark red solution, on dilution and acidification with hydrochloric acid, gave an orange red dye, which could be separated into mono- (III) and disazo (II) dyes as in the previous case; about 0·12 g. of the pure monoazo and 0·1 g. of the disazo dye were obtained.

4-Benzeneazo-2-acetyl-1-naphthol (*VI*)

The bright red dye, prepared in the usual manner from acetonaphthol and diazobenzene chloride, crystallised from acetic acid or chlorobenzene in reddish orange needles, m.p. 143° (Found: N, 9·8. $C_{18}H_{14}O_2N_2$ requires N, 9·7%). It gives a deep brown colour with ferric chloride and a violet colour with concentrated sulphuric acid.

4-Benzeneazo-2-acetyl-1-naphthyl benzoate (*VII*)

The dye (VI) (2 g.), pyridine (10 c.c.) and benzoyl chloride (1·5 g.) were refluxed for six hours in the oil-bath at 140°. The solution was poured over crushed ice and hydrochloric acid. The dark red sticky product was taken up in ether, washed with ice-cold dilute hydrochloric acid, water, and finally with ice-cold sodium carbonate solution. Removal of the solvent and crystallisation from alcohol gave orange prismatic needles (1·7 g.), m.p. 153° (Found: N, 7·1. $C_{25}H_{18}O_3N_2$ requires N, 7·2%).

4-Benzeneazo-2-benzoylacetyl-1-naphthol (*III*)

A mixture of the benzoate (1 g.), toluene (20 c.c.) and potassium carbonate (4 g.) was refluxed for 8 hours. The dark red potassium salt was filtered, washed with benzene and decomposed with dilute acetic acid. The brownish

red diketone (0·65 g.) crystallised from acetic acid or alcohol-acetic acid in short orange rods, m.p. 201–2° (Found: N, 7·4. $C_{25}H_{18}O_3N_2$ requires N, 7·2%). A mixed m.p. with the monoazo dye (III) obtained by direct coupling of the diketone showed no depression.

6-*Benzeneazo*-7: 8-*benzoflavone* (*IV*)

4-Benzeneazo-2-benzoylacetyl-1-naphthol (III) (0·2 g.) was refluxed with glacial acetic acid for 30 minutes, and cooled. The flavone (IV) crystallised in shining yellow needles, m.p. 271° (Found: N, 7·2. $C_{25}H_{16}O_2N_2$ requires N, 7·4%). The substance does not give a ferric chloride colour and is insoluble in aqueous or alcoholic alkali.

Treatment of the dye (III) with cold concentrated sulphuric acid also yielded the same flavone (IV).

4-*Nitro*-2-*acetyl*-1-*naphthyl benzoate* (*VIII*)

4-Nitro-2-acetyl-1-naphthol (2·5 g.), prepared by the nitration of 2-acetyl-1-naphthol with 40% nitric acid at room temperature, pyridine (15 c.c.) and benzoyl chloride (1·5 c.c.) were heated on the water-bath for 30 minutes and the solution poured over ice and hydrochloric acid. The semi-sticky solid which separated was taken up in ether washed with dilute hydrochloric acid, water and cold sodium carbonate solution respectively, the ether extract dried and the solvent removed. The semi-sticky solid crystallised from alcohol in short colourless plates (1·5 g.), m.p. 126–27° (Found: N, 4·0. $C_{19}H_{13}O_5N$ requires N, 4·2%).

6-*Acetamido*-7: 8-*benzoflavone* (*IX*) was obtained by reduction of the flavone (IV) with zinc dust in acetic acid solution. It crystallised from acetic acid in small lustrous, yellow needles, which melted with darkening in colour at 306–7° (Found: N, 4·3. $C_{21}H_{15}O_3N$ requires N, 4·2%).

6-*Amino*-7: 8-*benzoflavone* (*X*)

(i) The benzeneazoflavone (IV) (0·5 g.) was suspended in alcohol (30 c.c.), Raney nickel catalyst added and shaken with hydrogen under pressure (40 lbs.) for two hours when the flavone slowly went into solution. The catalyst was filtered off and the yellow filtrate diluted with water, the product which separated (0·25 g.) crystallised from alcohol in long, shining yellow needles, m.p. 220° (Found: N, 4·6. $C_{19}H_{13}O_2N$ requires N, 4·8%). It dissolves in concentrated sulphuric acid giving a colourless solution with a bright bluish violet fluorescence.

(ii) The dye (III) (0·1 g.), dissolved in alcohol (20 c.c.) and 10% sodium hydroxide solution (1 c.c.) was warmed to about 70°, and reduced by sodium

hydrosulphite till the colour of the solution changed from deep red to yellowish red. After heating for a few minutes, the solution was acidified with dilute acetic acid, concentrated and cooled. The aminoflavone (X) crystallised from alcohol in long, shining yellow needles.

Coupling of the diketone (I) with diazotised 2:5-dichloroaniline

The diketone (I) (0·5 g.), dissolved in pyridine (20 c.c.) was coupled in the usual manner with one mole. of diazotised 2:5-dichloroaniline. The dye, precipitated by dilution and acidification with hydrochloric acid, crystallised from acetic acid in fluffy aggregates of red needles (0·2 g.), m.p. 215–16° (Found: N, 8·9. $C_{31}H_{18}Cl_4O_3N_4$ requires N, 8·9%). The disazo dye (II; $C_6H_3Cl_2$ instead of Ph) gives a light brown colour with ferric chloride. The filtrate, after separation of the disazo dye, on dilution and crystallisation, gave the unreacted diketone (0·2 g.).

The diketone (I) (0·5 g.) dissolved in alcoholic sodium carbonate solution was then coupled with one mol. of diazotised 2:5-dichloroaniline. The dye was boiled in acetic acid (50 c.c.) and a small quantity of a yellowish-orange solid which separated was immediatey filtered off. It crystallised from a large volume of acetic acid in thin yellow rods (30 mg.), m.p. 295–96° (Found: N, 6·4. $C_{25}H_{14}Cl_2O_2N_2$ requires N, 6·2%). It does not give any ferric chloride colour and is not soluble in aqueous or alcoholic alkali. Analysis and its properties indicated that it was the flavone (IV, $C_6H_3Cl_2$ instead of Ph). From the acetic acid mother liquor, the disazo dye (0·2 g.) was obtained.

4-(2′:5′-*Dichloro*)-*benzeneazo*-2-*acetyl*-1-*naphthol* (*VI*; $C_6H_3Cl_2$ *instead of Ph*).

Acetonaphthol was coupled with diazotised 2:5-dichloroaniline, and the red dye crystallised from chlorobenzene in long needles, m.p. 229–30° (Found: N, 8·1. $C_{18}H_{12}Cl_2O_2N_2$ requires N, 7·8%).

4-(2′:5′-*Dichloro*)-*benzeneazo*-2-*acetyl*-1-*naphthyl benzoate* (*VII*; $C_6H_3Cl_2$ *instead of Ph*)

The dye (VI; $C_6H_3Cl_2$ instead of Ph) was benzoylated by refluxing with benzoyl chloride in pyridine. The benzoate crystallised from alcohol in yellowish orange needles, m.p. 184–5° (Found: N, 6·1. $C_{25}H_{16}Cl_2O_3N_2$ requires N, 6·0%).

6-(2′:5′-*Dichloro*)-benzeneazo-7:8-*benzoflavone* (*IV*; $C_6H_3Cl_2$ *instead of Ph*)

The benzoate on treatment with potassium carbonate in toluene rearranged to the yellowish red diketone (III; $C_6H_3Cl_2$ instead of Ph), m.p. 238–40°, which was converted into the corresponding flavone (IV; $C_6H_3Cl_2$

tnsead of Ph) by treatment with boiling glacial acetic acid, when it crystallised in thin yellow rods, m.p. 295–96° (Found: N, 6·3. $C_{25}H_{14}Cl_2O_2N_2$ requires N, 6·2%), identical with the corresponding flavone obtained by direct coupling of the diketone with diazotised 2: 5-dichloraniline followed by treatment with acetic acid.

ω-Benzeneazo-ω-benzoyl-1-acetyl-2-naphthol (*XII*)

The diketone (XI) (0·3 g.), prepared by the rearrangement of 1-acetyl-2-naphthol benzoate with sodium ethoxide,[4] was dissolved in alcohol (20 c.c.) and sodium acetate (1 g.) added, when the solution became greenish in colour. The solution was cooled and coupled with one mol. of diazotised aniline. The orange dye was filtered (0·3 g.), which crystallised from alcohol in small orange plates, m.p. 162° (Found: N, 7·2. $C_{25}H_{18}O_3N_2$ requires N, 7·2%). It gives a deep brown colour with ferric chloride.

4-Amino-2-acetyl-1-naphthol (*XIII*)

2-Acetyl-1-naphthol (5 g.) was dissolved in aqueous sodium hydroxide solution and coupled with diazotised metanilic acid (5 g.). The deep red coloured alkaline solution of the dye was heated to 70°, and hydrosulphite (9 g.) was slowly added till the colour of the solution became pale yellow. The orange crystalline amine which separated (3·5 g.) crystallised from dilute alcohol in orange needles, m.p. 122–23° (Found: N, 6·9. $C_{12}H_{11}O_2N$ requires N, 7·0%). It gave a brown colouration with ferric chloride.

4-Benzamido-2-acetyl-1-naphthyl benzoate (*XIV*)

4-Amino-2-acetyl-1-naphthol (XIII) (3 g.) in pyridine (10 c.c.) was mixed with benzoyl chloride (6 c.c.) and refluxed for 30 minutes. The yellow product (3 g.), obtained on stirring the solution into dilute hydrochloric acid, crystallised from alcohol in colourless needles, m.p. 175–6° (Found: N, 3·2. $C_{26}H_{19}O_4N$ requires N, 3·4%).

4-Benzamido-2-benzoylacetyl-1-naphthol (*XV*)

(XIV) (1 g.), anhydrous potassium carbonate (4 g.) and benzene (15 c.c.) were refluxed for 8 hours, the orange potassium salt filtered and stirred into dilute acetic acid and the product which separated was filtered. It crystallised from glacial acetic acid in orange needles, m.p. 232° (Found: N, 3·2. $C_{26}H_{19}O_4N$ requires N, 3·4%).

6-Benzamido-α-naphthaflavone (XVI), obtained by treatment of (XV) with cold concentrated sulphuric acid, crystallised from glacial acetic acid in plates, m.p. 273° (Found: N, 3·2. $C_{26}H_{17}O_3N$ requires N 3·6%).

4-*Acetoacetamido*-2-acetyl-1-naphthol (XVII)

4-Amino-2-acetyl-1-naphthol (XIII) (3 g.) and acetoacetic ester (3 c.c.) were refluxed for 6½ hours in chlorobenzene (25 c.c.) with a few drops of one N caustic soda solution. The residue, after distilling off chlorobenzene, was dissolved in caustic soda and reprecipitated by acid. The product (1·5 g.) crystallised from alcohol (Norit) in long yellow needles, m.p. 183°. (Found: N, 4·6. $C_{16}H_{15}O_4N$ requires N, 4·9%). It gives a dark green colour with ferric chloride.

2-*Acetyl*-4-*benzamidophenol* (*XVIII*)

4-Benzamidophenyl acetate (7 g.) was dissolved in dry acetylene tetrachloride (70 c.c.), aluminium chloride (10 g.) added and the mixture heated for 2 hours at 140–45°. The solution was stirred into ice and hydrochloric acid and carbon tetrachloride steam distilled. The yellow product (4 g.) crystallised from alcohol (Norit) in colourless needles, m.p. 155°. (Found: N, 5·2. $C_{15}H_{13}O_3N$ requires N, 5·5%). It gives a blue colour with ferric chloride.

ω-Benzoyl-2-*hydroxy*-5-*benzamidoacetophenone* (*XIX*)

2-Acetyl-4-benzamidophenyl benzoate was obtained by refluxing (XVIII) for 1½ hours with benzoyl chloride in pyridine. It crystallised from alcohol in colourless needles, m.p. 168–69° (Found: N, 3·8. $C_{22}H_{17}O_4N$ requires N, 3·9%).

2-Acetyl-4-benzamidophenyl benzoate (4·6 g.), benzene (100 c.c.) and sodamide (5 g.) were refluxed for 4 hours and the yellow product that separated was treated with dilute hydrochloric acid. It crystallised from glacial acetic acid in yellow needles, m.p. 210°. (Found: N, 3·8. $C_{22}H_{17}O_4N$ requires N, 3·9%). It gives an olive brown colour with ferric chloride.

The flavone (XX), obtained by treatment of the diketone (XIX) with cold concentrated sulphuric acid, crystallised from alcohol in colourless plates, m.p. 291° (Found: N, 4·1. $C_{22}H_{15}O_3N$ requires N, 4·1%).

Summary

The utility, as azoic coupling components, of diketones prepared by the action of sodamide and similar reagents on *o*-benzoyloxyaryl methyl ketones has been investigated. 2-Benzoylacetyl-1-naphthol gives weak dyeings when used as a "naphthol" for impregnation of cotton, and development with diazonium salts. The shades lacked fastness to soaping and light. On coupling the diketone in substance with diazonium salts, mono- and disazo dyes were obtained; the constitution of the former, which could

have two possible structures, has been proved to be 4-benzeneazo-2-benzoyl-acetyl-1-naphthol by an unambiguous synthesis from 4-benzeneazo-2-acetyl-1-naphthol through the corresponding benzoate. The monoazo dye from 1-benzoylacetyl-2-naphthol has been prepared. 4-Benzamido-2-benzoyl-acetyl-1-naphthol and 4-acetoacetamido-2-acetyl-1-naphthol have also been studied as "naphthols".

We are grateful to Imperial Chemical Industries (Dyestuffs Group) and to the Sir Dorab Tata Trust for the award of research fellowships to two of us. We are also thankful to Mr. T. S. Gore for carrying out the microanalyses.

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CHEMOTHERAPY OF BACTERIAL INFECTIONS

XII. Synthesis of Some Sulphanilamide and Sulphone Derivatives of Thiazole

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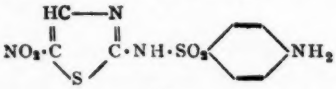
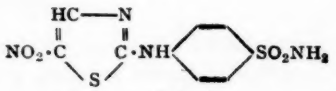
As a sequel to the discovery of the remarkable therapeutic properties of 2-sulphanilamidothiazole, we undertook the synthesis and study of all possible sulphanilamido derivatives of thiazole. Derivatives of 2-sulphanilamidothiazole with alkyl substituents at the positions 4 and 5 of thiazole and N^3 of the tautomeric thiazoline have previously been reported from this laboratory.[1] Herein we report the synthesis and study of more derivatives of this group, which were completed many years ago.

The condensation of acetsulphanilylchloride with 2-amino-5-nitrothiazole[2] and 2-amino-4-methyl-5-nitrothiazole[2] to obtain the 2-acetsulphanilamido derivatives could not be effected. To obtain this compound by the alternative method, 2-bromo-5-nitro-thiazole[3] was condensed with sulphanilamide in the presence of potassium carbonate and copper powder, a condition under which only the sulphonamide grouping has been established to react.[4] The reaction in this case was unusually vigorous. Of the numerous experiments tried under a variety of conditions, the required 2-sulphanilamido-5-nitrothiazole (I) could be isolated in only one experiment in bad yield. The use of acetyl sulphanilamide in the place of sulphanilamide in the above reaction did not lead to any better results. On the other hand, the condensation of 2-bromo-5-nitrothiazole with sulphanilamide in alcoholic solution, a condition under which the amino group is known to react,[4] furnished the isomeric product (II) in good yields.



(I)

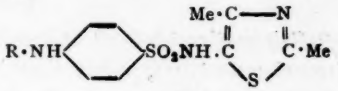


(II)

In the pyridine series, the three possible isomeric compounds with the sulphanilamido radical substituted at the positions 2, 3 and 4 of the pyridine ring have been synthesised and studied.[5] In the pyrimidine series also, the 2, 4 and 5 substituted sulphanilamido derivatives have been synthesised and

studied.[6] But at the time the present work was started, the sulphanilamido derivatives of thiazole substituted in positions 4 and 5 were not known. Arnold and Scaife[7] reported the synthesis of 5-sulphanilamidothiazole starting from chrysean. Jensen and Hansen[8] reported independently the synthesis of 2:4-dimethyl-5-sulphanilamidothiazole. We have attempted the synthesis of a number of 4- and 5-sulphanilamido derivatives. 2-Hydroxy-4-methyl-5-aminothiazole[3] condensed with acetsulphanilylchloride to yield 2-hydroxy-4-methyl-5-acetsulphanilamidothiazole (III) but this could not be deacetylated to the corresponding sulphanilamido derivative. 2:4-Dimethyl-5-amino-thiazole[3] condensed with acetsulphanilylchloride to yield 2:4-dimethyl-5-acetsulphanilamidothiazole (IV, R = Ac.), whose melting point

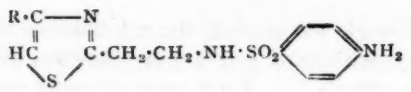
(III)



(IV)

does not agree with that given by Jensen and Hansen[8]; however, the deacetylated sulphanilamido derivative (IV, R = H) has the same melting point as that given by Jensen and Hansen. Contrary to the property of the 2-acetsulphanilamidothiazoles, the 5-acetsulphanilamidothiazole derivative is soluble in dilute acid. 2:4-Dimethyl-5-sulphanilamidothiazole has been tested in experimental Pneumococcal (Type I) and *P. pestis* infections in mice; it has about the same activity as sulphathiazole but it shows some peculiar toxic symptoms. The results of these experiments will be published elsewhere.

A few derivatives in which sulphanilamide radical is attached to the thiazole ring through one or two carbon atoms were prepared. Synthesis of such derivatives in the pyridine series have been reported[9] but there is no information available on their therapeutic properties. 2-Methylthiazole and 2:4-dimethylthiazole condensed with sulphanilamide in the presence of formalin to yield the two compounds V, R = H and Me respectively. Since the amino group is free in both these compounds (as revealed by the diazo-reaciton), the condensation has taken place through the sulphonamide radical. In the case of 2:4-dimethylthiazole, the 4-methyl group is established to be inert[13] and so the formula V is assigned to the condensation product. 2-Hydroxy-4-methylthiazole similarly reacted with sulphanilamide in the presence of formalin and the compound obtained is assigned the structure (VI) in view of the known behaviour of the thiazole derivatives.[14] None of these compounds showed any significant therapeutic activity in experimental Pneumococcal (Type I) infections in mice.



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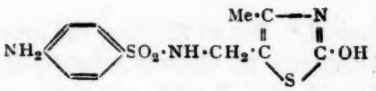

(VI)

p-Aminophenylsulphones of thiazole have previously been studied.[10] Herein the nature of the substituent has been found to influence the therapeutic activity. So by condensing *p*-acetaminobenzenesulphinic acid with 2-halogenothiazole derivatives a number of sulphones have been prepared which are described in the experimental portion. But none of them has been found to be of any value in experimental pneumococcus or plague infections in mice.

Experimental

2-*Sulphanilamido*-5-*nitrothiazole* (I).—An intimate mixture of 2-bromo-5-nitrothiazole (1 g.), sulphanilamide (0·9 g.), anhydrous potassium carbonate (·35 g.) and copper powder (0·3 g.) was heated at 100°. The reaction was unusually vigorous and was over in a few minutes. The dark coloured reaction product was powdered and extracted with boiling water. The deep red aqueous extract yielded nothing on neutralisation. The residual solid was then extracted with hot alcohol which yielded about 0·3 g. of yellow solid which did not crystallise but was purified by dissolving in dilute alkali, or ammonia, and then neutralising with acid; m.p. 245° (Found: N, 18·31. $C_9H_8O_4N_4S_2$ requires N, 18·67%). The presence of a free amino group in this compound was established by the diazo reaction.

2-(N^4-*Sulphanilamido*)-5-*nitrothiazole* (*II*).—2 - Bromo - 5 - nitrothiazole (4·2 g.) and sulphanilamide (3·45 g.) were refluxed in alcohol (25 c.c.) for 30 minutes. On cooling, deep yellow crystals separated which were collected and dried (yield, 4 g.). A further quantity of 1·7 g. was recovered from the filtrate. On recrystallisation from alcohol or glacial acetic acid, it had m.p. 258–9° (Found: N, 18·38. $C_9H_8N_4O_4S_2$ requires N, 18·67%). This compound easily undergoes decomposition when an alkaline solution is allowed to stand for sometime.

2-*Hydroxy*-4-*methyl*-5-*acetsulphanilamidothiazole* (*III*).—2- Hydroxy - 4 - methyl-5-aminothiazole (2 g.) in pyridine (5 c.c.) and acetone (10 c.c.) was treated with acetsulphanilylchloride (4 g.) under cooling. The mixture was carefully warmed at 50° C. for 15 minutes and then allowed to stand for 2 hours. On dilution with water (50 c.c.), a pinkish solid separated which was filtered, washed with water (yield, 2 g.) and crystallised from a mixture of pyridine and alcohol when it has m.p. 206° (dec.) (Found: N, 13·37. $C_{12}H_{13}N_3O_4S_2$ requires N, 12·84%).

2:4-*Dimethyl-5-acetsulphanilamidothiazole* (*IV*, $R = Ac$).—Crude 2:4-dimethyl-5-aminothiazole (5·3 g.) in dry pyridine (12 c.c.) was treated with acetsulphanilylchloride (11·8 g.). The reaction mixture was allowed to stay at the room temperature for 2 to 3 hours and then diluted with ice water. The crude product obtained (6 g.) was purified by dissolving in alkali (charcoal) and precipitating with acetic acid. On crystallisation from alcohol it separated in thick plates and had m.p. 220° (Found: N, 12·75. $C_{13}H_{15}O_3N_3S_2$ requires N, 12·92%). Jensen and Hansen[8] report m.p. 175° for this compound. This compound is soluble in dilute hydrochloric acid in contrast to the 2-acetsulphanilamidothiazole derivatives which are insoluble in dilute acids.

2:4-*Dimethyl-5-sulphanilamidothiazole* (*IV*, $R = H$).—The above described crude acetyl derivative (6 g.) was hydrolysed with dilute hydrochloric acid (60 c.c. of 4·5 N) under the usual conditions. This yielded the deacetylated product (4·3 g.) which on crystallisation from dilute alcohol or boiling water separated in thin plates and had m.p. 183° (Found: N, 14·68. $C_{11}H_{13}N_3O_2S_2$ requires N, 14·83%). Jensen and Hansen[8] give m.p. 183°.

2-*Methylthiazole*.—McLean and Muir[11] have stated that they could not prepare 2-methylthiazole from dichlorether and thioacetamide. We have, however, prepared it by this method though in bad yields.

A solution of thioacetamide (10 g.) in alcohol (20 c.c.) was treated with dichlorether (20 c.c.) in small quantities at a time under cooling (when the temperature was allowed to rise or the reaction product heated, the yield was further reduced). The reaction product was allowed to stand for 15 minutes, diluted with water (50 c.c.) and acidified with concentrated hydrochloric acid. The aqueous solution was decanted off from the pitchy product, extracted with ether, cooled, basified, the oil that separated taken up in ether and worked up as usual. The oil obtained of fractionation yielded 2-methylthiazole, b.p. 127–30° (yield, 2·7 g.).

2-β-(p-*Aminobenzenesulphonamido*)-*ethylthiazole* (*V*, $R = H$).—A mixture of 2-methylthiazole (2·7 g.) and finely powdered sulphanilamide (4·3 g.) in xylene (20 c.c.) was maintained at 120–125° and treated with paraformaldehyde (1·3 g.) in the course of 15 minutes. The reaction mixture was stirred well with a glass rod and the reaction was completed by heating for further 5 minutes. After decanting off the xylene the resulting hard mass was powdered and thoroughly extracted with ether and hot water. The compound was purified by dissolving it in alkali and precipitating with dilute acids (yield, 5·1 g.). It could not be crystallised from the usual organic

solvents; m.p. 237–38° (Found: N, 14·66. $C_{11}H_{13}N_3O_3S_2$ requires N, 14·84%).

4-Methyl-2-β-(p-aminobenzenesulphonamido)-ethylthiazole (V, R = Me).— This was prepared as the above described compound by treating a mixture of 2:4-dimethylthiazole (5 g.) and finely powdered sulphanilamide (7·6 g.) in xylene (35 c.c.) with *para*-formaldehyde (3 g.). The compound obtained (8·5 g.) could not be crystallised from the usual organic solvents but was purified by dissolving it in alkali and neutralising with acid; m.p. 241–42° (Found: N, 14·23. $C_{12}H_{15}O_2N_3S_2$ requires N, 14·14%.)

4-Methyl-2-β-(p-acetaminobenzenesulphonamido) ethylthiazole.— This compound was prepared as described above by using acetsulphanilamide in the place of sulphanilamide. It was purified by dissolving it in alkali and precipitating with acid; m.p. 211° (Found: N, 12·44. $C_{14}H_{17}O_3N_3S_2$ requires N, 12·39%). This compound caused no depression with that obtained by acetylating 4-methyl-2-(*p*-aminobenzenesulphonamido)-ethylthiazole with acetic anhydride.

2-Hydroxy-4-methyl-5-(p-aminobenzenesulphonamido) methylthiazole (VI). An intimate mixture of 2-hydroxy-4-methylthiazole (2·3 g.), sulphanilamide (3·4 g.) and anhydrous zinc chloride (1·0 g.) was warmed at 50–60° with formalin (10 c.c.) for 2 hours. The thick sticky mass was cooled, powdered, washed with boiling water and dried. The compound (5·7 g.) was purified by dissolving in alkali and neutralising with acid. The amorphous white solid obtained turns yellow at 200°, then brownish and melted at 224–27° (Found: N, 13·77. $C_{11}H_{13}N_3O_3S_2$ requires N, 14·04%).

p-Acetaminobenzene-2-(4: 5-dimethyl)-thiazolyl sulphone.—(i) 2-Chloro-4: 5-dimethylthiazole (3 g.) and potassium acetaminobenzene sulphinate (4·7 g.) in alcohol (15 c.c.) were refluxed for 4 hours. After removing the alcohol, the residue was diluted with water (20 c.c.) and the unreacted chlorothiazole extracted with ether. The crystalline white solid (0·25 g.) obtained was washed with water and dried. On recrystallisation from acetic acid it was obtained in rectangular plates and had m.p. 236° (Found: N, 9·12. $C_{13}H_{14}O_3N_2S_2$ requires N, 9·03%).

(ii) The chlorothiazole (3 g.) and the potassium salt (4·7 g.) were heated at 160–70° for 3 hours. The reaction mass, after washing with water and ether, was crystallised from boiling acetic acetic acid when it was obtained in glistening rectangular plates, m.p. 236° (yield, 3·5 g.). The ether washing gave back the unreacted chlorothiazole derivative.

(iii) The chloro compound (4·5 g.) and *p*-acetaminobenzene sulphinic acid (6 g.) in pyridine (20 c.c.) were heated for 4 hours. After dilution with water, the reaction product was filtered, washed free from pyridine with water and ether, and recrystallised from acetic acid (yield, 4 g.).

p-*Aminobenzene*-2-(4 : 5-*dimethylthiazolyl*) *sulphone*.—The above mentioned acetamino compound (3·0 g.) dissolved in glacial acetic acid (10 c.c.) was refluxed with dilute hydrochloric acid (5 c.c. of 1 : 1) for 90 minutes and the deacetylated product was precipitated by dilution. On crystallisation from an excess of boiling alcohol it separated in colourless plates and had m.p. 195° (Found: N, 10·23. $C_{11}H_{12}O_2N_2S_2$ requires N, 10·45%); yield, 2 g.

p-*Acetaminobenzene*-2-(5-*ethylthiazolyl*) *sulphone*.—2 - Chloro -5 - ethyl - thiazole (5 g.) and potassium *p*-acetaminobenzenesulphinate (7·1 g.) were heated at 170–80° for 4 hours. The fused mass was washed with water and then with ether. On crystallising the residue from 50% acetic acid, the sulphone melted at 172° (Found: N, 8·98. $C_{13}H_{14}O_3N_2S_2$ requires N, 9·03%); yield, 4·5 g.

p-*Aminobenzene*-2-(5-*ethylthiazolyl*) *sulphone*.—The above described acetyl compound (2 g.) was boiled with acetic acid (10 c.c.) and hydrochloric acid (10 c.c. of 1 : 1) for one hour. On diluting the resulting solution, the aminosulphone crystallised out. On recrystallisation from dilute alcohol, it was obtained in thick rhombic prisms and had m.p. 150° (Found: N, 10·31. $C_{11}H_{12}O_2N_2S_2$ requires N, 10·45); yield 1·4 g.

p-*Acetaminobenzene*-2-(5-*nitrothiazolyl*) *sulphone*.—To a solution of 2-bromo-5-nitrothiazole (10·5 g.) in boiling alcohol (75 c.c. of 50%) was added potassium acetaminobenzenesulphinate (13 g.). The condensation product separated out almost immediately as lemon yellow needles. The mixture was refluxed for 15 minutes more, the solid separated by filtration, washed with water and ether (yield, 15·6 g.). On recrystallising from glacial acetic acid, it had m.p. 200° (Found: N, 12·78. $C_{11}H_9O_5N_3S_2$ requires N, 12·84%).

p-*Aminobenzene*-2-(5-*nitrothiazolyl*) *sulphone*.—The above described acetyl compound (7·0 g.) in dilute acetic acid (50 c.c. of 1 : 1) was boiled under reflux with concentrated hydrochloric acid (7 c.c.) for 30 minutes. The deacetylated product separated as a deep yellow crystalline solid. The mixture was diluted with water and the amino compound collected after several hours. It was recrystallised from a mixture of dioxane and alcohol; the microcrystalline product obtained had m.p. 229° (Found: N, 7·72. $C_{15}H_{16}O_5N_2S_2$ requires N, 7·61%); yield, 3·6 g.

We thank Major-General Sir Sahib Singh Sokhey for his kind interest in these investigations and also the Lady Tata Memorial Trust for the award of a scholarship to one of us (A.V.).

Summary

Condensation of 2-bromo-5-nitrothiazole with sulphanilamide yielded (i) in the presence of potassium carbonate and copper powder, 2-sulphanilamido-5-nitrothiazole and (ii) in alcoholic solution the isomeric N^4- (5-nitro-2-thiazolyl)-sulphanilamide. 2-Hydroxy-4-methyl-5-aminothiazole and 2:4-dimethyl-5-aminothiazole condensed with acetsulphanilylchloride to yield respectively 2-hydroxy-4-methyl-5-acetsulphanilamidothiazole and 2:4-dimethyl-5-acetsulphanilamidothiazole. The latter, on hydrolysis, furnished 2:4-dimethyl-5-sulphanilamidothiazole, which was about as active as sulphathiazole in experimental pneumococcal and *P. pestis* infections in mice but much more toxic. By condensing 2-methylthiazole, 2:4-dimethylthiazole and 2-hydroxy-4-methylthiazole with formalin and sulphanilamide, were obtained respectively 2-β-(*p*-aminobenzenesulphonamido) ethylthiazole, 4-methyl-2-β-(*p*-aminobenzenesulphonamido) ethylthiazole and 2-hydroxy-4-methyl-5- (*p*-aminobenzenesulphonamido) methylthiazole, none of which showed any therapeutic activity in experimental pneumococcal infections in mice. Condensation of potassium acetaminobenzenesulphinate with 2-chloro-4:5-dimethylthiazole, 2-chloro-5-ethylthiazole and 2-bromo-5-nitrothiazole, the corresponding 2-*p*-acetaminobenzene sulphonylthiazoles were obtained which were deacetylated to the corresponding amino compounds; these compounds also did not show any striking therapeutic activity.

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CHEMOTHERAPY OF MALARIA

Part I. A Study of the Methods of Synthesis of Diguanides

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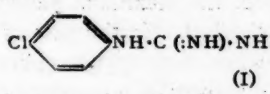
The present state of knowledge of the problem of malaria, and the targets of the chemotherapy of malaria have been discussed elsewhere.[1] The present communication forms a part of the work undertaken along those lines. Of the thousands of compounds studied in recent years, only the 8-aminoquinolines and N^1-*p*-chlorophenyl-N^5-*iso*propyldiguanide (paludrine, I) have been found to possess significant action on the exoerythrocytic form of *Plasmodium vivax* to be of any practical value. While the 8-aminoquinolines have little margin of safety, the action of paludrine is not intense enough. We have undertaken the synthesis of hybrids of these two structures to see if their properties could be reinforced in the same compound. In the synthesis of quinoline compounds with the substituted diguanide side chain, the problem initially turned out to be one of developing suitable methods for the construction of the required N^5-substituted side chain. So, we explored the various methods of synthesis of N^1 : N^5-disubstituted diguanides, taking paludrine (I) as the model compound. This paper presents some of the results obtained.



(I)

Paludrine consists of two guanidine units linked in series and so the methods of synthesis of the guanidines could be used for its synthesis by choosing appropriate reactants. The three standard methods that can be employed for the synthesis of the guanidines are as follows:

(i) $R \cdot NH \cdot CN + NH_2R' \rightarrow R \cdot NH \cdot C(:NH) \cdot NH \cdot R'$ (Erlenmeyer's synthesis[2])

(ii) $R \cdot NH \cdot C(:NH) \cdot SMe + NH_2R' \xrightarrow{-HSMe}$

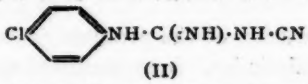
$R \cdot NH \cdot C(:HR') \cdot SMe + NH_3 \xrightarrow{-HSMe}$ } Rathke's synthesis[3, 5]

(iii) $R \cdot NH \cdot CS \cdot NH_2 + NH_2R' \xrightarrow{-H_2S}$

$R \cdot NH \cdot CS \cdot NH \cdot R' + NH_3 \xrightarrow{-H_2S}$ } 4

Many permutations and combinations are possible with these three methods and we have tried a number of them in which the reactants are easily accessible.

At the time the work was started, two methods of syntheses of paludrine had been published. The first one based on the work of Slotta and Tschesche[6] was worked out by Curd and Rose[7] and consisted of the condensation of *p*-chlorophenyldicyandiamide (II) with isopropylamine. This method has

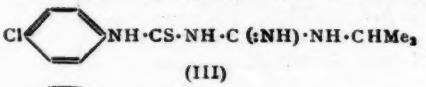


(II)

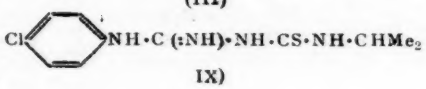
been studied in detail in this Institute and has been found to be the best and cheapest for the large-scale manufacture of this drug. We have found that N^1-*p*-chlorophenyl-N^5-*iso*propyldiguanide (I) on crystallisation from dilute alcohol separates in colorless needles which melt at 96–97°, solidify and then melt again at 125–6°. Only the latter melting point has been recorded by Curd and Rose[7] who crystallised this compound from toluene. The other method is due to Dasgupta and Basu[8] which consists in the condensation of *p*-chlorophenylguanidine with *iso*propylcyanamide.

Choosing as one reactant *iso*propylguanidine sulphate, which was easily prepared by the condensation of *iso*propylamine with S-methylthiourea sulphate, we tried three methods by condensing it with (1) *p*-chlorophenylcyanamide, (2) S-methyl *p*-chlorophenylisothiourea and (3) *p*-chlorophenylthiourea. In all these three cases the required N^1-*p*-chlorophenyl-N^5-isopropyldiguanide (I) was obtained, the maximum yield being obtained in the first case and the minimum in the last. In the case of the condensation with *p*-chlorophenylcyanamide, when *iso*propylguanidine sulphate was used in the place of the free guanidine derivative, a compound, m.p. 125–6°, but not identical with the required diguanide (I) was obtained in poor yields. When this work was completed, we came to know that patent applications have been filed by the Imperial Chemical Industries, Limited, covering substantially the same processes.

Attempts were next made to prepare the two compounds, N′-(*p*-chloroanilinothioformyl)-N″-*iso*propylguanidine (III) and N′-(*p*-chlorophenyl)-N″-(*iso*propylaminothioformyl) guanidine (IV), and then to replace the sulphur atom in them by the imino groups by known methods.[4,5] But so

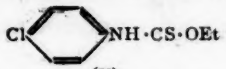


(III)



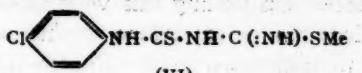
IX)

far, we have not succeeded in preparing either of these two compounds, though a number of methods were tried. Condensation of *p*-chlorophenylisothiocyanate with *iso*propylguanidine in alcoholic solution furnished a product, m.p. 104·5–5·5°, which was identified to be *p*-chlorophenylthiourethane (V). In benzene solution, no condensation product



(V)

could be isolated. Similarly, phenylguanidine also did not condense with *iso*propylisothiocyanate. This confirms the conclusion of Slotta, Tschesche and Dressler[9] that the mustard oils condense with guanidine and *syn*diphenylguanidines but not with mono-substituted guanidines. The condensation of *p*-chlorophenylcyanamide with either thiourea or *iso*propylthiourea furnished only the polymerised products of *p*-chlorophenylcyanamide. *p*-Chlorophenylisothiocyanate condensed easily with isomethylthiourea to yield S-methyl-N-(*p*-chloroanilino) thioformylisothiourea (VI), m.p. 134·5–5° Attempts to replace the methylmercapto group in this compound by the amino or substituted amino groups led to unexpected changes. On boiling the compound with alcoholic ammonia, *p*-chlorophenylthiourea was obtained. By using *iso*propylamine in the place of ammonia under a variety of conditions, three products were isolated: (1) a compound, m.p. 125–6°, identified to be *p*-chlorophenyl*iso*propylthiourea (VII), (2) a compound, m.p. 157–8° which appears to be *p*-chlorophenylcyanthiourea (VIII) and (3) a compound, m.p. 203–5°, which has not been identified.



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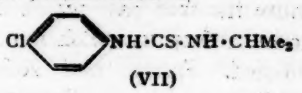

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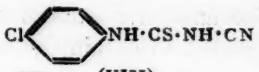
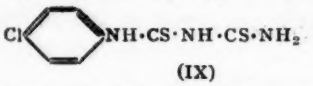


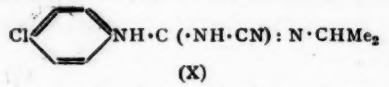
(VIII)

Attempts were then made to prepare compounds of type (III) through the phenyldithiobiuret derivative. On condensing two molecular equivalents of *p*-chloraniline with isopersulphocyanic acid, *p*-chlorophenyldithiobiuret (IX), m.p. 163–4°, was obtained. On boiling this compound with two molecular equivalents of mercuric oxide and ammonia, *p*-chlorophenyldicyandiamide (II) was obtained in good yields. This method is of particular interest because in the case of many amines, particularly the heterocyclic compounds not easy to diazotise, the dicyandiamide derivative could be prepared by this route. We have actually applied this to prepare quinoline derivatives and the results obtained will be published in due course. But in the attempts to prepare a compound replacing only the end thioamide

group by the amidine group by using only one molecular equivalent of mercuric oxide and ammonia, the only crystalline compound isolated was the diacyandiamide derivative. On boiling *p*-chlorophenyldithiobiuret with two molecular equivalents of mercuric oxide and *iso*propylamine, N-*p*-chlorophenyl-N′-isopropyl-N″-cyanoguanidine (X), m.p. 151·5°, was



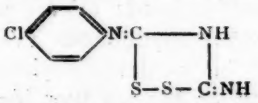
(IX)



(X)

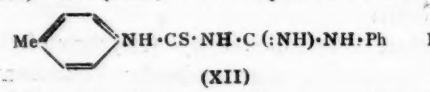
obtained. In this case also, using one molecular equivalent of mercuric oxide and *iso*propylamine, the anticipated compound (III) was not isolated. In *p*-chlorophenyldithiobiuret, the end thioamide group gets easily converted into the cyano group in the presence of desulphurising agents and it is not possible to replace the sulphur atom by the imino group. On the other hand, the sulphur atom in the thioamido group near the benzene ring undergoes this replacement quite easily. Thus, we have a good method of preparing compounds of formula (X) which we are utilising for the synthesis of many substituted diguanides by condensing them with the appropriate amines.

p-Chlorophenyldithiobiuret on oxidation with iodine in alcoholic solution yielded the hydroiodide of *p*-chlorophenylthiuret (XI). We could not



(XI)

crystalise the free base which is unstable. On boiling this with alcoholic ammonia, a deep seated change took place and no crystalline product could be isolated. Fromm and Veller[10] have condensed *p*-methylphenylthiuret with aniline and *p*-toluidine and have isolated the two isomeric products (XII) and (XIII). We expected to obtain the compound (III) by boiling



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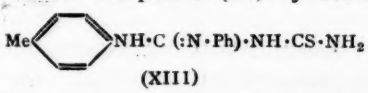
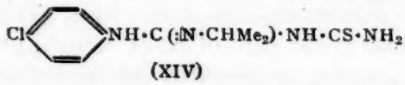


(XIII)

p-chlorophenylthiuret with *iso*propylamine. Instead, the only compound isolated was found to be the isomer, N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine (XIV). The structure of this is confirmed since this com-



(XIV)

pound on boiling with mercuric oxide in alcoholic solution furnished N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine (X). On boiling the compound (XIV) with alcoholic ammonia and mercuric oxide, surprisingly

enough, *p*-chlorophenyldicyandiamide (II) was obtained, the isopropylamino group being replaced by the imino group. The isopropyl group in the compound (X), however, is not replaced by boiling with alcoholic ammonia. Boiling *p*-chlorophenylthiuret with alcoholic ammonia and mercuric oxide yielded *p*-chlorophenyldicyandiamide, while by using *iso*propylamine in the place of ammonia, we obtained N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine (X).

Thus, in our work on the dithiobiuret and thiuret derivatives, though we did not succeed in preparing the compound (III), we have evolved a good method of preparing the dicyandiamide derivatives, which are particularly useful in preparing heterocyclic derivatives.

Experimental

Iso*propylguanidine sulphate*.—To S-methyl*iso*thiourea sulphate (30 g.) dissolved in the minimum amount of water, *iso*propylamine (20 c.c.) was added with shaking and the mixture refluxed cautiously for 3 hours and then vigorously for seven hours more, when the evolution of methylmercaptan almost ceased. The solution was evaporated to a syrup and lixiviated with alcohol, when *iso*propylguanidine sulphate separated from the mixture in a crystalline form (yield, 25 g.). It was collected and recrystallised from alcohol. The compound separated in needles and was very hygroscopic, m.p., 225–6°. (Found: N, 27·32; 27·4. $C_4H_{10}N$, 1/2 H_2SO_4 requires N, 28·1%.)

N[1]-p-*Chlorophenyl-N*[5]-iso*propyldiguanide* (*I*).—(i) The paper of Curd and Rose[7] does not contain exact details for the preparation of this compound and we have effected a number of improvements in this process which is being run on a pilot plant scale in this Institute.

To *p*-chlorophenyldicyandiamide (2 g.) in alcohol (40 c.c.) was added a solution of copper sulphate (1·6 g.) in water (6 c.c.) with good shaking so that the copper salt separated in a finely divided form. To this, *iso*-propylamine (2 c.c.) was added and the mixture refluxed on the steam bath for four hours, when the green copper salt had turned completely pink. The alcohol was then evaporated off and the residue triturated with dilute hydrochloric acid (6 c.c. of con. acid diluted with 30 c.c. water), when practically all the copper salt went into solution. The filtered clear solution was treated with a concentrated solution of sodium sulphide, the copper sulphide filtered off, and the clear solution basified with a solution of sodium hydroxide when the diguanide derivative separated in a crystalline form (yield, 1·8 g.). On crystallisation from dilute alcohol, it separated in clusters of fine needles,

m.p. 96–7° (solidifies and then melts again at 125–6°). This sample gave no depression in m.p. on admixture with a commercial sample similarly crystallised.

(ii) Sodium (0·3 g.) was dissolved in butyl alcohol (20 c.c.) and to this *iso*propylguanidine sulphate (3·8 g.) was added and shaken well. To the mixture, *p*-chlorophenylcyanamide (1·9 g.) was added and refluxed for 3 hours. The resulting mixture was diluted with ether (200 c.c.) and extracted with dilute hydrochloric acid (75 c.c. of 1 : 3). The acid extract after clarification with charcoal was basified with a solution of sodium hydroxide when the diguanide derivative separated as an oil and gradually solidified to a crystalline mass (yield, 1·5 g.). On crystallisation from dilute alcohol, it separated as a mass of fine crystalline needles, m.p., 96–97°, and was found to be identical with the product obtained in experiment (i). Alternatively, the butyl alcohol was steam distilled off and the resulting acid solution basified. But the product obtained by this proceedure was not as pure as that obtained by acid extraction.

(iii) Sodium (0·4 g.) was dissolved in butyl alcohol (50 c.c.) and to this *p*-chlorophenyl*iso*methylthiourea hydroiodide (3·4 g., prepared by the action of methyl iodide on *p*-chlorophenylthiourea) and *iso*propylguanidine sulphate (3·0 g.) were added, the mixture refluxed for 4 hours and worked up as above described, whereby 1·0 g. of the diguanide derivative was obtained. In this experiment sodium bicarbonate was used in the place of sodium but the yield was considerably less than when sodium was used.

(iv) A mixture of *iso*propylguanidine sulphate (2·9 g.), *p*-chlorophenylthiourea (3·0 g.) and lead oxide (4·5 g.) in butyl alcohol (50 c.c.) was refluxed for six hours with good shaking. The mixture was filtered, the lead sulphide washed with butyl alcohol and the combined butanol solution worked up as indicated above, when about 0·25 g. of the diguanide derivative was obtained.

p-Chlorophenylthiourethane (*V*).—This compound was obtained by refluxing *p*-chlorophenyl*iso*thiocyanate for thirty minutes in alcoholic solution. It crystallised from dilute alcohol in beautiful needles and had m.p. 104–5·5°. (Found: N, 6·09; 6·20. $C_9H_{10}NSCl$ requires N, 6·49 per cent.). This compound was identical with that obtained when *p*-chlorophenyl*iso*thiocyanate was refluxed with *iso*propylguanidine in alcoholic solution.

S-Methyl-N-(p-chloroanilino)-thioformylisothiourea (*VI*).—To isomethylthiourea sulphate (4·9 g.) dissolved in water (20 c.c.) was added sodium bicarbonate (2·9 g.) followed by acetone (40 c.c.); to the solution *p*-chlorophenylisothiocyanate (4·8 g.) was added and the mixture refluxed for about

two hours. The mixture which had separated into two layers was allowed to evaporate and the crystalline product that separated was collected (7·2 g.) and recrystallised from dilute alcohol. The condensation product was obtained in prismatic needles and had m.p. 134·5–135° (dec.). (Found: N, 16·05. $C_9H_{10}N_3S_2Cl$ requires N, 16·18 per cent.).

Action of alcoholic ammonia on S-methyl-N-(p-*chloroaniline*)*-thioformyl-*iso*thiourea.*—S-Methyl-N-(*p*-chloroanilino)-thioformylisothiourea (1·0 g.) in alcoholic ammonia (50 c.c.) was gently refluxed for four hours and the solution evaporated to dryness. The residue on crystallisation from alcohol, yielded a product crystallising in thin needles, m.p. 175–76·5°. (Found: N, 14·9; 15·1. *p*-Chlorophenylthiourea, $C_7H_7N_2SCl$, requires N, 15·02 per cent.), which showed no depression in m.p. on admixture with a genuine sample of *p*-chlorophenylthiourea.

Action of iso*propylamine on S-methyl-N-*(p-*chloroanilino*)*-thioformyl-*iso*thiourea.*—To S-methyl-N-(*p*-chloroanilino)-thioformylisothiourea (1 g.) in alcohol (20 c.c.) were added water (5 c.c.) and *iso*propylamine (2 c.c.); the mixture was refluxed for three hours, the solution evaporated to dryness and the residue crystallised from a mixture of benzene and little alcohol. A product crystallising in plates, m.p. 157–8°, (Found: N, 19·6; 20·1; 19·8 per cent.) was obtained, which appears to be *p*-chlorophenylcyanothiourea ($C_8H_6N_3SCl$ requires N, 19·85 per cent.).

In the above experiment, when a large excess of *iso*propylamine was used and the time of refluxing prolonged, two other products were obtained: (1) a compound crystallising in needles, m.p. 202·5–3° (Found: N, 16·75; 16·55; 16·8; 17·03 per cent.) and (2) a compound crystallising in fine needles, m.p. 124–5°, which was identified to be *p*-chlorophenyl*iso*propylthiourea by comparing it with a specimen prepared as indicated below.

*p-Chlorophenyl*isothiocyanate.—This compound was prepared by Losanitch[11] by the action of iodine on bis-(*p*-chlorophenyl)-thiourea. The following method is a rapid one but the yield is only about 30 per cent. of the theoretical.

To *p*-chloroaniline (40 g.) suspended in alcohol (75 c.c.) and ammonium hydroxide (75 c.c.), was added carbon disulphide (45 c.c.) with good shaking. When the mixture warmed up, it was cooled in ice-bath. A clear solution was obtained and then the crystalline ammonium dithiocarbamate derivative separated. It was allowed to stand overnight, the crystalline product filtered, dissolved in water (about 1 litre) and a solution of lead nitrate (100 g.) added and the mixture subjected to steam distillation. *p*-Chlorophenyl*iso*thiocyanate passed over as an oil and solidified as a snow white crystalline mass; m.p. 46–7° (yield, 19 g.).

Iso*propyl*iso*thiocyanate*.—The preparation of this compound has been reported by Jahn[12]; the following method gives a better yield. *Iso*propylamine (84 c.c.) in water (150 c.c.) was cooled in an ice-bath and carbon disulphide (60 c.c.) was run in and shaken well. To this, under cooling, a solution of sodium hydroxide (40 g.) in water (230 c.c.) was added gradually in the course of about half an hour. A white precipitate separated. After allowing the mixture to stand for about two hours more, water was added to dissolve the crystalline solid, followed by a concentrated solution of mercuric chloride (136 g.). After shaking the mixture well, it was subjected to steam distillation. *Iso*propyl*iso*thiocyanate passed over as an oil; it was collected and fractionated; b.p. 138° (yield, 38 g.).

*N^1-Chlorophenyl-N^5-iso*propylthiourea (*VIII*).—This compound was obtained by refluxing (1) *p*-chlorophenyl*iso*thiocyanate with *iso*propylamine and (2) *p*-chloraniline with *iso*propyl*iso*thiocyanate, in alcoholic solution. On crystallisation from dilute alcohol it separated in beautiful needles, m.p. 124–5°. (Found: N, 12·17. $C_{10}H_{13}N_2SCl$ requires N, 12·26 per cent.)

p-Chlorophenyldithiobiuret (*IX*).—A mixture of *iso*persulphocyanic acid (3·0 g.) and *p*-chloraniline (5·1 g.) in alcohol (75 c.c.) was refluxed for two hours. The yellow *iso*persulphocyanic acid gradually disappeared and a crystalline product separated. The mixture was cooled, the solid obtained dissolved in cold 5 per cent. sodium hydroxide solution to free it from the accompanying sulphur, filtered and the clear filtrate acidified with concentrated hydrochloric acid whereby the condensation product separated as a bulky mass. It was separated by filtration (yield, 2·3 g.) and crystallised from dilute alcohol, whereby *p*-chlorophenyldithiobiuret separated in clusters of fine needles, m.p. 163–4°. (Found: N, 17·23; 17·41. $C_8H_8N_3S_2Cl$ requires N, 17·1 per cent.)

Action of alcoholic ammonia and mercuric oxide on p-*chlorophenyldithiobiuret*.—*p*-Chlorophenyldithiobiuret (2 g.) in alcoholic ammonia (50 c.c.) and mercuric oxide (3·8 g.) was refluxed on the steam-bath. The yellow oxide rapidly turned black. After refluxing for about four hours, it was filtered, the alcohol evaporated from the filtrate and the residue crystallised from dilute alcohol. The compound crystallising in thin leaflets, m.p. 202–3°, was identified to be *p*-chlorophenyldicyandiamide by comparing it with an authentic specimen.

In the above experiment, even when one molecular equivalent of mercuric oxide was used, the only product that could be isolated in crystalline form was the same *p*-chlorophenyldicyandiamide.

Action of iso*propylamine and mercuric oxide on p-chlorophenyldithiobiuret.*—*p*-Chlorophenyldithiobiuret (2 g.) in alcohol (50 c.c.) and *iso*propylamine (5 c.c.), was treated with mercuric oxide (3·8 g.) and the mixture refluxed on the steam-bath for four hours. The black precipitate was filtered off and the filtrate evaporated to dryness. On crystallisation from alcohol, a product separating in rectangular plates, m.p. 151·5°, (Found: N, 23·68 per cent.), was obtained which was identified to be N-*p*-chlorophenyl-N′-isopropyl-N″-cyanoguanidine (X) (see below).

p-*Chlorophenylthiuret* (*XI*)*-hydroiodide.*—*p*-Chlorophenyldithiobiuret (10 g.) in alcohol (100 c.c.) warmed to obtain a solution and to this a concentrated solution of iodine (10 g.) in alcohol was added till the decolorisation was complete and a faint colour of iodine was permanent. A bulky crystalline precipirate separated which rapidly became granular. This was cooled, filtered and washed with alcohol. The hydroiodide of *p*-chlorophenylthiuret thus obtained (10 g.) was used as such without any further purification.

Action of alcoholic ammonia and mercuric oxide on p-*chlorophenylthiuret.*—*p*-Chlorophenylthiuret hydroiodide (2 g.) in alcoholic ammonia (50 c.c.) was treated with mercuric oxide (1·8 g.) and the mixture gently refluxed for 3 hours. The black precipitate was filtered off, and the mother liquor, on working up as usual, furnished a product crystallising in thin plates, m.p. 202–3°, which showed no depression in m.p. on admixture with *p*-chlorophenyldicyandiamide.

Action of iso*propylamine and mercuric oxide on* p-*chlorophenylthiuret.*—In the above experiment when *iso*propylamine was used in the place of alcoholic ammonia, a compound, m.p. 150–1°, was obtained which was identified to be N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine.

N-(p-*Chlorophenyl*)-*N′*-iso*propyl-N″-aminothioformylguanidine* (*XIV*).—*p*-Chlorophenylthiuret hydroiodide (15 g.) suspended in alcohol (50 c.c.) was treated with *iso*propylamine (15 c.c.) and the mixture boiled for three hours. The alcohol was distilled off and the residue boiled with a small quantity of water and filtered hot to free it from the sulphur accompanying the product. From the filtrate, the condensation product crystallised out in fine plates (yield, 7 g.). On repeated crystallisation from water, it had m.p. 153–4·5°. (Found: N, 21·02; 21·12; 20·99; 21·19. $C_{11}H_{15}N_4SCl$ requires N, 20·70 per cent.)

p-*Chlorophenyl-N′*-iso*propyl-N″-cyanoguanidine* (*X*).—The abovementioned compound (0·5 g.) dissolved in alcohol (20 c.c.) was treated with mercuric oxide (0·6 g.) and the mixture refluxed for about three hours. The black precipitate was filtered off and the residue on working up yielded the

desulphurised product which crystallised from dilute alcohol in shining prisms and had m.p. 150–151·5°. (Found: N, 23·72; 23·94; 23·75. $C_{11}H_{13}N_4Cl$ requires N, 23·67 per cent.)

Action of alcoholic ammonia and mercuric oxide on the compound (*XIV*).—In this experiment, the compound that was isolated crystallised from alcohol and had m.p. 201–2° (Found: N 29·2. *p*-Chlorophenyldicyandiamide. $C_8H_7N_4Cl$. requires N, 28·6 per cent.) showing no depression in m.p. on admixture with a genuine sample of *p*-chlorophenyldicyandiamide.

Action of alcoholic iso*propylamine and mercuric oxide on the compound* (*XII*).—In this case, the compound isolated was identified to be N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanoguanidine.

We are indebted to Mr. M. H. Shah of the Department who carried out the analyses recorded in this paper. We also thank Major-General Sir Sahib Singh Sokhey for his kind interest in these investigations.

Summary

In the course of attempts to prepare quinoline derivatives with substituted diguanide side chains, the methods of syntheses of N^1-*p*-chlorophenyl-N^5-*iso*propyldiguanide (I) as a model compound have been investigated. The diguanide (I) was obtained by the condensation of *iso*propylguanidine with (1) *p*-chlorophenylcynamide, (2) S-methyl-*p*-chlorophenyl*iso*thiourea and (3) *p*-chlorophenylthiourea in the presence of lead acetate. Attempts to prepare the compound (III) by the condensation of *p*-chlorophenyl*iso*-thiocyanate with *iso*propyl guanidine were unsuccessful. *p*-Chlorophenyl-*iso*thiocyanate condensed with S-methyl *iso*thiourea to yield S-methyl-N^1-(*p*-chloroanilino)-thioformyl*iso*thiourea (VI but the methylmercapto group of this compound could not be replaced by either imino or *iso*propylimino groups. *p*-Chloraniline condensed with *iso*persulphocyanic acid to yield *p*-chlorophenyldithiobiuret which on boiling with ammonia and *iso*propylamine in the presence of mercuric oxide furnished respectively *p*-chlorophenyldicyandiamide and N-*p*-chlorphenyl-N′-*iso*propyl-N″-cyanoguanidine (X). *p*-Chlorophenyldithiobiuret on oxidation with iodine yielded *p*-chlorophenylthiuret which on treatment with ammonia and *iso*propylamine in the presence of mercuric oxide furnished respectively *p*-chlorophenyldicyandiamide and N-*p*-chlorophenyl-N′-*iso*propyl-N″-cyanguanidine. On treatment with *iso*propylamine, *p*-chlorophenylthiuret yielded only N-(*p*-chlorophenyl)-N′-*iso*propyl-N″-aminothioformylguanidine (XII), which easily undergoes desulphurisation to yield the compound (X); however, in the presence of alcoholic ammonia and mercuric oxide, *p*-chlorophenyldicyanamide was obtained.

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A NEW EFFECT OF HYDROGEN BOND FORMATION (CHELATION)

Part III. Isomerization of Rottlerone Analogous to Rottlerin-Iso-Allorottlerin (Isorottlerin) Change

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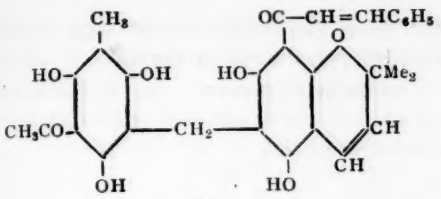
The isomerization of rottlerin into iso-allorottlerin (isorottlerin) was observed by a number of workers.[1,2,3]. Brockmann and Maier[1] considered it to consist of the cyclisation of the chalkone form into the flavanone. Mcgookin, Robertson and Tittensor[3] later showed that it was not a simple chalkone-flavanone change but involved further an interchange of the cinnamoyl and the substituted phloroglucinol residues. In their extremely careful and clear study of this interesting isomeric change, they expressed the opinion that it can best be explained on the view that the first stage of the reaction is the conversion of rottlerin (I) into the intermediate (II) by the opening of the chromene ring system and that this is followed by the reformation of the latter to produce (III) which is strictly analogous to rottlerin and termed allorottlerin. At the same time, the chalkone is cyclised to dihydro- *r*-pyrone system with the production of type (IV) which they regarded as representing Brockmann and Maier's isorottlerin and which they appropriately designated iso-allo-rottlerin. From the intermediate allorottlerin, two formulæ for the cyclisation product (IV and V) are possible but owing to lack of evidence a decision between the two orientations could not be made by them.

The most important and valuable point which the above authors have definitely made out is the shift of the chromene ring. The reason as to why this takes place has not so far been clear. Some light seems to be thrown on this question by the recent work of Narasimhachari and Seshadri[4] on a new effect of hydrogen bond formation. In their paper, the importance of a 5-hydroxyl for the stability of a flavanone structure has beeen brought out. It arises from the formation of a chelate ring involving the carbonyl group and the 5-hydroxyl. If there were no shift of the chromene ring and only the flavanone ring closure took place, a 7-hydroxyflavanone derivative (VI) would have resulted. But on account of the rearrangement of the chromene ring a 5-hydroxyflavanone derivative (IV or V) is obtained and this represents a more stable structure. The reason for the iso-allorottlerin change



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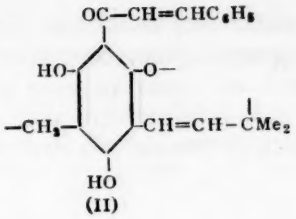

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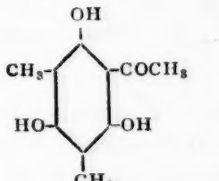

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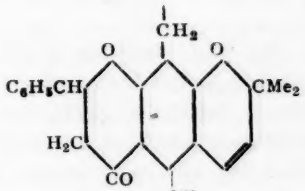

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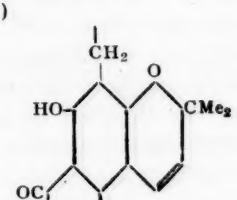
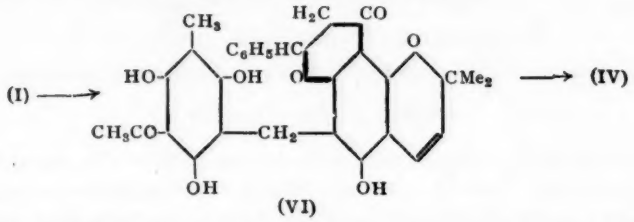


(V)

would therefore appear to be that thereby the molecule reaches greater stability.

Based on the above considerations it would be simplest to picture that the flavanone ring closure which generally proceeds readily in acid solutions, takes place first yielding the 7-hydroxy flavanone derivative (VI) and then the rearrangement of the chromene ring follows producing the stabler 5-hydroxy flavanone derivative. The constitution of isoallorottlerin then becomes reasonably certain as in (IV). But Robertson and his coworkers who recognised this possibility were not inclined to accept it because they felt that the closing of the dihydro-γ-pyrone ring involving the protection of a free hydroxyl

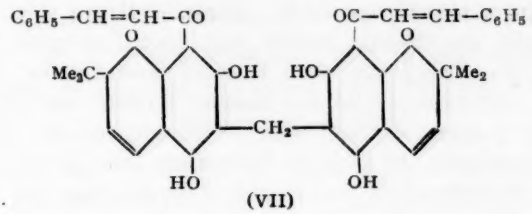
group would tend to stabilise the chromene system and would thus hinder rearrangement. Some unequivocal evidence is therefore required to settle this point and it does not seem to be available at present. But at the same time it should be borne in mind that even in chalkones the ortho-hydroxyl is not entirely free and it is involved in a chelate ring.



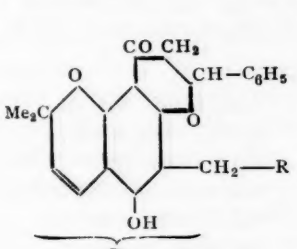
(VI)

No other example of this type of rearrangement seems to have been described in the literature. A closely analogous substance suitable for this study is rottlerone (VII), the main degradation product of rottlerin. Its constitution has been definitely established by Robertson and his co-workers[5] and it has all the structural features required for this test. In the past, Brockmann and Maier[1] reported that they did not get any definite reaction product by refluxing rottlerone with acetic acid. Mcgookin *et al.*[5] noticed that a yellow amorphous substance was formed under these conditions but stated that they had been so far unable to determine conditions required for cyclisation of rottlerone and the isolation of the resulting pure dihydro-γ-pyrone derivative. We have again examined this reaction. Rottlerone undergoes change almost completely by boiling its acetic acid solution for one hour. The deep red colour of rottlerone disappears and a pale yellow product is obtained in good yield. For it the name iso-allorottlerone is suggested. It could not be crystallised satisfactorily from any solvent, but could be obtained as an almost colourless (very pale yellow) crystalline powder from glacial acetic acid solution, by the addition of water. Though its melting point too is not very definite, it is clear that the isomeric change has taken place. The very pale yellow colour of iso-allorottlerone as contrasted with the highly coloured rottlerone is in agreement with the flavanone structure and the colour reaction with ferric chloride (immediate deep green colour) supports the presence of a hydroxyl group in the 5-position of each of the flavanone units. A hydroxyl in the 7-position does not give rise to any colour with ferric chloride. There is no possibility of attributing this ferric chloride colour to contamination with rottlerone because it gives an entirely different colour (brown). Iso-allorottlerone can therefore be considered to have a 5:5′-dihydroxy-diflavanone structure (IX). The isomeric change

taking place is very similar to the change of rottlerin into iso-allorottlerin, the possible intermediate 7-hydroxy flavanone stage being represented by (VIII).



(VII)



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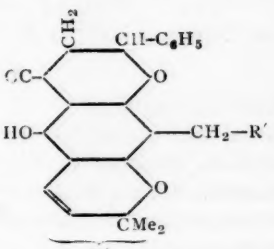

(IX)

Simpler and typical examples are further being investigated in order to test the validity of the above explanation of the isomeric changes.

Experimental

Rottlerone required for the following experiments was prepared from rottlerin using saturated barium hydroxide according to the method described by Mcgookin, Reed and Robertson.[6] It was obtained from chloroform-alcohol mixture in the form of garnet red prisms melting at 234–35°. It was very sparingly soluble in alcohol and insoluble in aqueous sodium carbonate solution. It was also insoluble in cold aqueous sodium hydroxide and on heating it decomposed forming a red coloured semi-solid, the solution turning yellow. With alcoholic ferric chloride, rottlerone gave first a very feeble brown colour which deepened on standing.

Iso-allorottlerone

Rottlerone (2 g.) and glacial acetic acid (50 c.c.) were heated on an oil-bath kept at 120–30° for one hour. By this time the initial bright red colour of the solution had completely changed to yellow. The solution was cooled and added to cold water and allowed to stand over night. The very pale yellow (almost colourless) substance that separated out was filtered and

dried. Attempts to crystallize the product from acetone-alcohol, ethyl acetate-petroleum ether and ether-petroleum ether mixtures were not successful. But in the course of these treatments, particularly the last, some amount of sparingly soluble impurity could be removed. It was then taken up in glacial acetic acid, the solution treated with animal charcoal, filtered and diluted with water. This process was repeated several times. A very pale yellow (almost colourless) crystalline looking powder was thus obtained. It was insoluble in aqueous alkali even on heating and did not show any signs of decomposition. It gave an immediate deep green colour with alcoholic ferric chloride which was entirely different from the colour given by rottlerone. On heating it sintered at 98° and melted down to a liquid at 140°. (Found: C, 75·0; H, 5·8; $C_{41}H_{39}O_8$ requires C, 75·0; H, 5·8%.)

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FORMATION OF QUINONES BY OXIDATIVE DEALKYLATION

Part III. Alkali Fission of Gardenin

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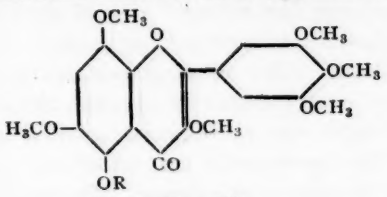
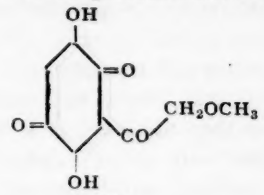
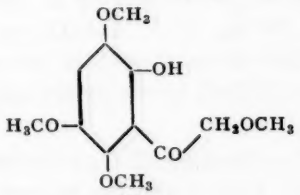
In the study of the constitution of flavones alkali fission is an important operation. The use of aqueous alkali or aqueous alcoholic alkali gives the acid product representing the side-phenyl nucleus fairly readily. It is not, however, satisfactory for the isolation of the ketonic product representing the fused benzene ring. Absolute alcoholic potash is much more useful. Even here only completely methylated or ethylated flavones undergo fission satisfactorily whereas partial ethers having free hydroxyl groups are resistant. Bose and Nath[1] reported that when gardenin, 5-hydroxy-3:6:8:3′:4′:5′-hexamethoxy-flavone (I, R = H), was boiled with 15 per cent. alcoholic potash, they obtained trimethyl gallic acid and a chocolate-coloured compound melting at 158–60° having only one methoxyl group and exhibiting quinone and acid properties. Subsequently Bose[2] drew attention to the similarity between this compound and 2:5-dihydroxy-quinones in general and pedicinin in particular and concluded that it should have the structure (II). Employing gardenin methyl ether (I, R = CH_3) for the alkali fission, Balakrishna and Seshadri[3] showed that the fission went smoothly yielding a tetramethoxy-monohydroxy-ketone (III). By the action of nitric acid it underwent oxidative demethylation to form a neutral quinone-ketone (IV).



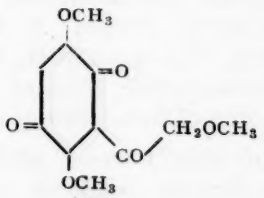
(I), R=H or CH_3



(II)



(III)



(IV)

It was felt necessary to study the observation of Bose and Nath in greater detail since it constituted a case of oxidative demethylation by means of alcoholic alkali, the intermediate stage being probably ω: 3 : 5-trimethoxy-2: 6-dihydroxyacetophenone. Our present work confirms their observation. Further the constitution of the product is established as (II) by its preparation by the alkaline hydrolysis of the methoxy-quinone-ketone (IV). It should be noted here that all the nuclear methoxyl groups in ketone (III) can be removed through the stages (IV) and (II) because they are all in susceptible positions.[4] Further alkali is required for the demethylation of (IV) in conformity with the behaviour of 1:2:4:5-tetramethoxybenzene derivatives.[4]

Expecting that the above described behaviour of gardenin with alcoholic alkali may be characteristic of partial methyl ethers of flavones with a free hydroxyl group in the 5-position a select number of analogous compounds having some of the features of gardenin have been studied. They are tetramethyl-ether of quercetin, pentamethyl ethers of myricetin, quercetagetin and gossypetin having a free hydroxyl in the 5-position and calycopterin having free hydroxyls in the 5- and 4′-positions. Surprisingly none of these underwent decomposition with alcoholic alkali under conditions when gardenin gave a good yield of the dihydroxy-quinone-ketone (II). Only their sparingly soluble potassium salts separated out and remained unaffected.

Experimental

ω-Methoxy-3: 6-dihydroxy-2: 5-quino-acetophenone (II):

(i) *Hydrolysis of ω: 3: 6-trimethoxy-2: 5-quino-acetophenone (IV).*—The trimethoxy-quino-acetophenone[3] (0·8 g.) was just warmed with 40 per cent. aqueous potash (2 mols.) till a clear solution was obtained and cooled. The potassium salt separated out as a red solid. After allowing to stand for an hour it was filtered and washed with a small quantity of absolute alcohol. It was then dissolved in a few c.c. of water and the aqueous solution was acidified with dilute sulphuric acid. The brown solid that separated out, was extracted with ether and the ether solution concentrated. The product crystallised from alcohol as chocolate-coloured prisms melting at 159–60°. Yield, 0·3 g. (Found: C, 51·1; H, 4·0; OCH_3, 14·8; $C_9H_8O_6$ requires C, 50·9; H, 3·8 and OCH_3, 14·6%). An alcoholic solution of the substance, which was initially coloured orange, changed to dark brown on the addition of a drop of ferric chloride solution.

(ii) *Alkali fission of gardenin (I, R = H).*—Gardenin (2·0 g.) was treated with alcoholic potassium hydroxide (15%, 40 c.c.) and the mixture was

refluxed for six hours. The solution was left overnight in the refrigerator. The brown potassium salt that separated out was filtered and washed with a little absolute alcohol. It was dissolved in a small volume of water and worked up as described in the previous experiment. The final product was identical in all respects with the compound obtained above and the mixed melting point was undepressed.

The fission could also be effected with 8% alcoholic potash; but then the reaction was not quite complete in 6 hours and required longer boiling for completion.

Summary

The observation of Bose and Nath regarding the fission of gardenin with alcoholic potash is confirmed. The formation of ω-methoxy-3: 6-dihydroxy-2: 5-quino-acetophenone (II) in this reaction constitutes an example of oxidative demethylation by means of alcoholic potash. The same compound can be obtained from methyl gardenin through the stages (III) and (IV). Analogous partial methyl ethers of flavones with a free 5-hydroxyl are resistant to this treatment.

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